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APPLICABILITY OF CATALYTIC OXIDATION TO THE DEVELOPMENT OF NEW PROCESSES FOR REMOVING SO_2 FROM FLUE GASES

Volume I – LITERATURE REVIEW

Contract No. PH 22-68-12

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Submitted to

Division of Process Control Engineering
National Air Pollution Control Administration
Environmental Health Services
U.S. Public Health Service
U.S. Department of Health, Education, and Welfare
5710 Wooster Pike
Cincinnati, Ohio 45277

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233

PB 198 808

BIBLIOGRAPHIC DATA SHEET	1. Report No. APTD-0675	2.	3. Recipient's Accession No.
4. Title and Subtitle Applicability of Catalytic Oxidation to the Development of New Processes for Removing SO_2 From Flue Gases Volume I - Literature Review			5. Report Date August 1970 6.
7. Author(s) R. E. Opferkuch, Project Leader, S. M. Mehta, A. H. Konstam, D. L. Zanders, H. R. Strop			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Monsanto Research Corporation Dayton Laboratory Dayton, Ohio 45407			10. Project/Task/Work Unit No. 11. Contract/Grant No. PH 22-68-12
12. Sponsoring Organization Name and Address Process Control Engineering Program National Air Pollution Control Administration Environmental Health Service, U.S. Dept. of HEW 5710 Wooster Pike Cincinnati, Ohio 45277			13. Type of Report & Period Covered 14.

15. Supplementary Notes

16. Abstracts

An extensive literature search for pertinent information relative to the catalytic oxidation of sulfur dioxide, is presented in this report. This, the first phase of the program, also attempts to identify, describe and evaluate processes, disclosed in the literature to have commercial potential for removal of sulfur dioxide from flue gas by oxidation.

17. Key Words and Document Analysis. 17a. Descriptors

Catalysis
Reaction kinetics
Oxidation
Sulfur dioxide
Catalysts
Vanadium
Magnesium Oxides
Electric Power plants
Flue gases

17b. Identifiers/Open-Ended Terms

Kiyoura process
Montsanto process
Mitsubishi process
Tyco process

17c. COSATI Field/Group 13/B

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Unlimited	UNCLASSIFIED	239
	20. Security Class (This Page) UNCLASSIFIED	22. Price

FORM NTIS-35 (10-70) USCOMM-DC 40329-P71

MRC-DA-245

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MRC Job No. 6708

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August 1970

Submitted to

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FOREWORD

The intent of this volume is to present in an organized manner the accumulation and assessment of all available literature data on SO_2 removal from flue gases by new and existing catalytic oxidation processes as of 31 December 1968. In that this volume represents the first phase of a three phase program of concurrent tenure, occasional reference to phases two and three will be seen at various points through the text. Further definition of these areas may be found in the respective volumes, each of which is reported under separate cover.

This final report is presented in three volumes in an effort to make the material accessible on the assumption that it is of practical value and therefore will be put to use.

Volume I is intended to contain all, and only, that material derived from, or related to, the literature search. Essentially all information in Volume I is directly based on the literature.

Volume II presents data and information generated in the laboratory and on the drawing board.

Volume III is an indexed bibliography.

Finally, guidance through the three volumes is offered in the form of the Foreword, Project General Summary and Tables of Contents in each of the three volumes.

The authors wish to acknowledge the many helpful comments and suggestions of the NAPCA Project Officer, Mr. George L. Huffman.

PROJECT GENERAL SUMMARY

The salient features of the project are summarized briefly below. Expansion and details are given in the texts of Volumes I and II.

The main objectives of the program were:

a. Search all available literature for pertinent information relative to the catalytic oxidation of sulfur dioxide, i.e., active materials, mechanisms of catalysis, methods of application, equipment employed, etc. Identify, describe and evaluate processes disclosed in the literature to have commercial potential for removal of sulfur dioxide from flue gas by oxidation.

b. Test, in the laboratory, candidate materials and methods suggested in the literature for potential application to removal of sulfur dioxide from flue gas by catalytic oxidation.

c. Identify at least one effective catalyst for the desired application and design a process for removal of sulfur dioxide from flue gas by catalytic oxidation and recovery of the sulfur value.

An intensive search of the literature revealed the following:

a. The transition metal oxides, notably vanadia, and platinum were the most commonly employed solid catalysts for practical conversion of sulfur dioxide to trioxide. Nitrogen dioxide was the only practical gaseous catalyst noted.

b. Kinetic equations describing conversions of sulfur dioxide over vanadia or platinum catalysts were derived from data relative to commercial production of sulfuric acid, i.e., high concentrations of sulfur dioxide. There was nothing available to describe results at the comparatively low concentrations of sulfur dioxide found in flue gas.

c. A number of processes were described as having commercial potential for flue gas cleaning. Comparative cost-performance evaluation of these oxidation processes eliminated all but two types as having realistic commercial potential, viz., one type based on vanadia catalyst and one based on nitrogen dioxide catalyst.

d. The most practical mode of recovery of oxidized sulfur value from a use standpoint, in this country, is production of fertilizer grade sulfuric acid.

Laboratory tests and comparative evaluation of commercial and experimental catalysts indicated the following:

a. Commercial vanadia catalysts employed in production of sulfuric acid are effective in converting sulfur dioxide at concentrations found in flue gas.

b. Although platinum catalyst performance is essentially equivalent to that of vanadia, a cost-performance comparison indicated vanadia is ten times more effective.

c. No other candidate materials were shown to be as effective as vanadia, platinum or nitrogen dioxide in converting sulfur dioxide to trioxide.

d. Nitrogen dioxide was the only practical "low temperature" catalyst observed.

e. Using nitrogen dioxide as a catalyst, it is potentially practical to remove both sulfur dioxide and indigenous nitrogen oxides from flue gas simultaneously.

From preliminary process designs and cost estimates, based on laboratory data generated in this program, the following emerge:

a. Processes, based on vanadia catalyst, for oxidizing sulfur dioxide and removing it from power plant flue gas, as sulfuric acid, are likely to cost in the range of $12 to $25 of capital per installed Kw of power plant capacity. A large portion of the cost results from the need for corrosion resistant equipment.

b. Operating costs for vanadia based processes are likely to be in the range of 0.50 to 0.74 mills/Kw-Hr generated before sulfur value net back.

c. A substantial reduction in capital and operating costs are potentially available through a technique of sorbing the oxidized product gas from the main flue gas stream and recovering it separately.

d. The vanadia based processes are better suited to proposed new power plant installations than to existing plants because of numerous difficulties in retro-fit to existing power plants.

VOLUME 1

TABLE OF CONTENTS

		Page
I.	SUMMARY	1
II.	CONCLUSIONS	4
III.	DISCUSSION	6
	A. INTRODUCTION	6
	B. CATALYSIS IN SO_2 OXIDATION	8
	1. General Remarks	8
	2. Factors Affecting Activity of Solid Catalysts	9
	3. Comparison of Platinum and Vanadium as Catalysts	11
	4. Conversion of SO_2 Under Equilibrium Conditions	14
	5. Conversion of SO_2 Under Non-Equilibrium Conditions	17
	a. Introduction	17
	b. Oxidation Over Vanadium Catalysts	18
	c. Oxidation Over Platinum Catalyst	35
	d. Oxidation of SO_2 on Chromium Oxide Catalyst	38
	e. Oxidation Over Iron Oxide Catalysts	39
	6. Catalyst Poisoning and Effects of Inert Gases	40
	7. Oxidation of SO_2 in an Electrical Discharge	42
	8. Feasibility of Photochemical and Radiation Methods for SO_2 Oxidation	43
	a. Introduction	43
	b. Direct Irradiation of SO_2-Containing Flue Gases	43
	c. Irradiation Pre-Treatment of Catalysts for SO_2-Oxidation	47
	9. Irradiation of SO_2 Containing Flue Gases in the Presence of Catalysts	49
	10. Liquid Phase Catalysis	49
	11. Homogeneous Gas Phase Catalysis	49

TABLE OF CONTENTS (Cont'd)

	Page
C. APPLIED CATALYSIS IN FLUE GAS TREATMENT	50
1. General	50
2. Vanadia Based Processes	51
a. Monsanto-Penelec Process	51
b. Kiyoura-T.I.T. Process	54
c. Bayer Double Contact Process	57
3. Carbon Based Processes	58
a. Reinluft Process	58
b. Sulfacid Process	61
c. Hitachi Process	63
4. Manganese Based Processes	65
a. Mitsubishi Process	65
b. TVA Ozone-Manganese Processes	68
5. Selenium-Based Process	69
a. Nor Deutsche Affinerie Process	69
b. Badische Anilin- and Soda-Fabrik Process	73
6. Modified Chamber Process	75
7. Reversible Dry Absorbant Process	77
8. Process Cost Estimates	79
9. Comparative Evaluation of Flue Gas Treatment Processes	83
References	105
Appendix I - Conversion Efficiency and Rate Equation Graphs	115
Appendix II - Mathematical Models and Computer Program Listings	133
Appendix III - Catalyst Data Sheets	155
Appendix IV - Capital Cost Sheets	219

LIST OF FIGURES

		Page
1	Computed Equilibrium Conversion Values	16
2	Results of Experiments of Boreskov, et al	28
3	Results of Eklund's Measurements	29
4	Results of Kinetic Measurements on Catalyst 3	30
5	Results of Kinetic Measurements on Catalyst 1 and 2	31
6	Monsanto-Penelec Process -- New Plant	52
7	Monsanto-Penelec Process -- Existing Plant	53
8	Kiyoura-T.I.T. Process -- New Plant	55
9	Kiyoura-T.I.T. Process -- Existing Plant	56
10	Reinluft Process for SO_2 Removal	59
11	Lurgi Sulfacid Process for SO_2 Removal	62
12	Hitachi Process for SO_2 Removal	64
13	Flow Diagram of Mitsubishi Manganese Dioxide Process	66
14	Flow Diagram of TVA Direct Sulfuric Acid Process	70
15	TVA Direct Ammonium Sulfate Process	71
16	Nor Deutsche Affinerie Process for SO_2 Removal	72
17	Badische Anilin- and Soda-Fabrik Process for SO_2 Removal	74
18	TYCO Modified Chamber Process	76
19	Callery Dry Absorbant Process	78
20	Effect of Product Credit on Operating Cost of Monsanto-Penelec Process (Existing Plant)	87
21	Effect of Product Credit on Operating Cost of Monsanto-Penelec Process (New Plant)	89
22	Effect of Product Credit on Operating Cost of Kiyoura-T.I.T. Process (Existing Plant)	91
23	Effect of Product Credit on Operating Cost of Kiyoura-T.I.T. Process (New Plant)	93
24	Effect of Product Credit on Operating Cost of Reinluft Process	95

LIST OF FIGURES

		Page
25	Effect of Product Credit on Operating Cost of Mitsubishi Process	99
26	Effect of Product Credit on Operating Cost of T.V.A. -- Direct Acid Process	101
27	Effect of Product Credit on Operating Cost of Callery Process	103

LIST OF TABLES

		Page
1	Catalysis and Promoters for the Oxidation of Sulfur Dioxide (Heterogeneous Catalysis)	9
2	Computed Equilibrium Conversion Values for $SO_2 + 1/2\ O_2 \leftrightarrows SO_3$	17
3	Effect of Contact Time on Conversion	18
4	Forms Used for the Function $f(P_{O_2}, P_{SO_2}, P_{SO_3})$	20
5	List of Rate Equations Used in Calculations	21
6	Catalysts Used to Obtain Rate Equations in Table 5	24
7	Rate Equations for the Oxidation of SO_2 Over Platinum Catalyst	37
8	Methods for Radiation Enhancement	44
9	Effect of Radiation Pretreatment of Catalysts for SO_2 Oxidation	48
10	Capital Requirements and Operating Costs for SO_2 Oxidation Processes	80
11	Operating Cost Estimate Summary - Monsanto-Penelec Process (Existing Plant)	86
12	Operating Cost Estimate Summary - Monsanto-Penelec Process (New Plant)	88
13	Operating Cost Estimate Summary - Kiyoura-T.I.T. (Existing Plant)	90
14	Operating Cost Estimate Summary - Kiyoura-T.I.T. (New Plant)	92
15	Operating Cost Estimate Summary - Reinluft Process	94
16	Operating Cost Estimate Summary - Sulfacid Process	96
17	Operating Cost Estimate Summary - Mitsubishi Process	98
18	Operating Cost Estimate Summary - T.V.A. Sulfuric Acid Process	100
19	Operating Cost Estimate Summary - Callery Process	102

I. SUMMARY OF LITERATURE REVIEW

The objective of Phase I of the program was to identify, by a comprehensive literature search, and to evaluate existing and potential methods of applying catalysis to the oxidation and removal of the sulfur dioxide in powerhouse stack gas.

The literature notes a large number of individual materials, and combinations of materials, as capable of converting sulfur dioxide to sulfur trioxide. Unfortunately, the experimental conditions, the conversion efficiencies, and the extrapolated economics for essentially all cases cited were impractical in relation to the present application. Among the numerous materials mentioned, the better ones consistently were vanadia (V_2O_5), platinum, oxides of iron, oxides of chromium, and carbon. Of these, the best, and only practical ones, were shown to be vanadia and platinum, and even platinum was shown to be economically impractical when compared with vanadia. This conclusion is not surprising considering the depth and breadth of the original research that culminated finally in the commercial vanadia catalysts now employed throughout the world for sulfuric acid production. Nor is it surprising considering the research effort expended during the past 30-odd years to produce a catalyst better than vanadia.

For an equally long period, the kinetics of sulfur dioxide oxidation and the catalytic mechanics have been studied by numerous researchers. Essentially all such studies were related to conversion with vanadia catalyst in gas streams containing 5-12% sulfur dioxide, typical of that in contact sulfuric acid plant operation. Some half-dozen kinetic equations are offered in the literature as descriptive of sulfur dioxide conversion data with vanadia catalyst in relatively narrow incremental ranges of conditions within the broad concentration range noted above. Nothing of the sort was found relative to conversion under conditions typical of the stack gas environment. Considerable divergence of opinion was found with regard to the mechanics of vanadia catalysis, particularly as to what constitutes the limiting step. There appeared to be more support for the proposal that re-oxidation of V^{4+} to V^{5+} is the limiting step than for any other proposal.

Five of the kinetic equations reported for use with vanadia were used to predict conversion efficiency at the concentration of sulfur dioxide representative of that in flue gas. Subsequently, data generated during the program with vanadia and simulated flue gas showed two of the equations to be quite accurate in their predictions for such conditions. These were an equation by Mars and Maessen and one by Eklund. The former, not having a factor to account for equilibrium, is very accurate in all regions below equilibrium and drifts

off as equilibrium is approached. Eklund's equation includes a response for equilibrium conditions and thus, while far less adequate in sub-equilibrium regimes, becomes progressively more descriptive as equilibrium is approached.

Based on the assumption that re-oxidation of vanadous oxide to vanadic oxide is the limiting reaction in the catalysis, a route is suggested to low temperature vanadia catalysis. It is known that the activity of commercial vanadia catalyst begins at the temperature at which the alkali pyrosulfate promoters begin to melt. It is also known that the vanadia dissolves in the molten pyrosulfates and it is assumed that such solubility is required for catalytic activity. If this is true, a pyrosulfate system melting at a lower temperature and dissolving vanadia should constitute an active catalyst system. The alternatives are (1) the re-oxidation reaction of V^{4+} to V^{5+} is extremely temperature dependent or (2) an entirely different mechanism acts at lower temperatures. The literature did not provide evidence to support or deny either of these alternatives.

The possibilities of enhancing catalytic activity through pretreatment of either the feed gas or the catalyst by various types of irradiation or by continuous irradiation of either were examined and found to be impractical for two reasons: (1) beneficial effects possible were transient and of low order; and (2) cost of treatment was prohibitive, irrespective of the effect.

The recent literature notes several processes, proposed for the removal of sulfur dioxide from powerplant stack gas ostensibly by catalytic oxidation. On examination, not all of these processes, at various stages of development, were found to involve catalysis in the true sense of the meaning. Those employing vanadia, manganous ion (in aqueous solution), and carbon were noted as being truly catalytic, while others employing dry manganese dioxide or selenium dioxide were noted as involving straightforward stoichiometric reactions between sulfur dioxide and the "catalyst."

All but two of the process types described in the open literature were found to be impractical, or extremely limited in applicability, on the basis of complexity (relating to capital and operating costs) and "Product" value. Product value here refers either to market value or to product disposal generally, i.e., substitution of one pollution problem for another. The two process types of potentially broad application are those employing vanadia and manganese dioxide. These processes are represented by the Kiyoura and Monsanto Company vanadia processes, producing ammonium sulfate and sulfuric acid, respectively; and, the Mitsubishi manganese dioxide process producing ammonium sulfate. As noted above, the latter process is non-catalytic, which leaves only one type of potentially practical catalytic process, namely, that employing vanadia catalyst.

The Tyco process for sulfuric acid production from power plant flue gases offers another possibility wherein SO_2 is converted via a homogeneous catalysis route using, in part, the NO_x contained in the flue gas effluent. The process is still in a developmental stage.

This review reflects only the processes reported in the literature prior to 31 December 1968. Subsequent developmental modifications and new process schemes are necessarily not evaluated.

Future developments in the application of oxidative catalysis to removal of sulfur dioxide are seen as evolving along the following lines:

(1) Development of a "low" temperature catalyst.

(2) Improvement in economics and applicability through engineering development.

(3) Inclusion of economical means of removing SO_2 from flue gas to supply a more concentrated feed stream to the catalytic converter.

(4) Inclusion of economical means for simultaneously removing the SO_2 and the NO_x present in the flue gas.

II. CONCLUSIONS FROM LITERATURE REVIEW

1. The materials consistently noted as effective in converting sulfur dioxide to trioxide are: V_2O_5, Pt, Cr_2O_3, Fe_2O_3, and C.

2. Only V_2O_5, Pt, and C show sustained high conversion activity below 500°C.

3. Although carbon appears to be active at temperatures below 400°C, no satisfactory method was noted for desorbing the conversion product from carbon.

4. No catalyst (other than carbon) was noted as having practical activity below 400°C.

5. The oxides of chromium and iron generally show sustained conversion activity at 600°C and above.

6. The oxides of iron, chromium, and vanadium are essentially "poison" resistant, while platinum is subject to poisoning by a variety of materials.

7. The activity of vanadia (V_2O_5) is maximized by promoting it with alkali pyrosulfate, notably potassium pyrosulfate.

8. The reactions of vanadia catalysis are believed to occur in a liquid (molten) phase of the pyrosulfate promoter in which the vanadia dissolves.

9. The rate controlling step in vanadia catalysis is believed to be re-oxidation of V^{+4} to V^{+5} by oxygen.

10. The kinetic equation by Mars and Maessen best fits the data on non-equilibrium oxidation of sulfur dioxide over vanadia catalyst under flue gas conditions; Eklunds kinetic equation best fits the data at equilibrium.

11. The rate controlling step in platinum catalysts is believed to be oxidation of sulfur dioxide by atomic oxygen.

12. The kinetic equation by Uyehara and Watson best fits the data on non-equilibrium oxidation of sulfur dioxide over platinum catalyst under flue gas conditions.

13. Theories relating catalyst activity to pore volume, surface area, lattice spacing, surface electronic effects etc., are often erroneous.

14. Potential methods for enhancing catalyst activity through irradiation by a variety of sources were shown to be impractical.

15. A vanadia based process appears to offer a practical means for removing sulfur dioxide from powerhouse stack gas by catalytic oxidation.

16. An adaptation of chamber process technology appears to offer the possibility of simultaneous removal of SO_x and NO_x and of retrofit to existing power plants (low temperature exhaust).

17. A process consisting of vanadia catalysis followed by a sorption step to remove and concentrate SO_3 appears to offer the possibility of improved economics compared to the condensation route to SO_3 recovery.

III. DISCUSSION

A. INTRODUCTION

This program was implemented by NAPCA with the objective of collecting and evaluating all available data in the literature relating to removal of sulfur dioxide from flue gases by existing or potential methods that employ catalytic oxidation with subsequent recovery of the sulfur value. There is a wealth of information in the literature concerning the catalytic conversion of sulfur dioxide to trioxide, but it is not directly related to the desired application.

Generally, the same materials that are effective as catalysts in many applications, namely, the transition metals, are noted as active in varying degree in effecting conversion of sulfur dioxide. There is, inevitably, some combination of these and assisting materials (promoters) that shows fair to good activity at some elevated temperature. However, also inevitably, the activities are lower than, or the temperatures are higher than, those associated with either platinum or vanadium catalysts. The primary reason for such divergence in behavior is connected with the stability of the sulfate of the element employed as catalyst. To behave as an effective catalyst, a material must release, or desorb, the conversion product, sulfur trioxide. The transition metal oxides form sulfates with sulfur trioxide and, except for vanadium, the decomposition temperatures of the sulfates are usually above 500°C, frequently above 600°C. At these temperatures, the conversion equilibrium begins to shift strongly to the left so that, added to whatever inherent lack of conversion activity these materials may have, is even poorer conversion inherent in the reaction itself. The sulfate of vanadium, however, is unstable even at room temperature, and platinum does not form the sulfate under conversion conditions.

Catalysis generally is viewed more as an art than a science, and this is reflected by two facets in the literature related to conversion of sulfur dioxide. The first is the almost infinite number of combinations of materials studied through the years for catalytic activity. The second is the almost amusing disagreement expressed regarding the mechanism of the catalytic action. Whatever the various views, however, essentially all of them relate to conversion in gas streams where the sulfur dioxide concentration is generally in the range of 5-12 vol % and not to powerhouse flue gas where the concentration is in the range of 0.05 to 0.5 vol %.

When the literature refers to conversion under flue gas conditions, it is describing one specific process among a number of processes that have been proposed in recent years and pursued to various stages of development. If a process was reported to produce a sul-

fate, the process was examined in our survey. This revealed that several of the processes were not truly catalytic, but since they were examined anyway, they are reported along with those that are truly catalytic.

Two NAPCA-sponsored processes are reported that were not in the open literature. These are a) the Tyco process, which applies Chamber Process Technology to flue gas cleaning, and b) the Callery Chemical Co. process which sorbs SO_2 from flue gas leaving a contact converter and delivers it in a concentrated stream to an absorption tower. Both processes are interesting, but are still in the laboratory stage.

Sulfur value is commonly recovered as sulfuric acid or ammonium sulfate. Overall economics appear to favor a heterogeneous catalytic process recovering sulfuric acid in a concentration range of 77-83% H_2SO_4. While some other product may be justified in particular instances, the potential supply of any product from this source could affect the disposal of the product. A vanadia contact process, for example, recovering sulfur value is ammonium sulfate, appears to afford attractive savings in capital cost. However, in the United States at least the product is essentially valueless and presents a disposal problem.

Finally, the practicality must be considered of integrating the sulfur dioxide removal process with the power production process. It is easy to visualize designing a new power plant to incorporate the flue gas treatment plant. Integration of the treatment process with existing power plant facilities, on the other hand, can only be custon-engineered for each application. For this reason, costs of such a treatment process for existing power stations can only be given in rather broad terms. In the future, another factor will affect treatment cost; it is the requirement to remov NO_x, or any other pollutant, in the same treatment process for removing sulfur dioxide. It must be recognized early that the power industry is not likely to be able to sustain a series of "black boxes" hooked on the exhaust end of a power plant. Consequently, for any flue gas treatment process, multifunctionality becomes an increasingly important consideration.

In the remainder of this report, the various aspects of the problems touched on above are discussed in greater detail.

B. CATALYSIS IN SO_2 OXIDATION

1. General Remarks

The reactions for producing sulfur trioxide and sulfuric acid have been known for several centuries. One early reference, cited the production and isolation of sulfur trioxide by Albertus Magnus in the 13th Century (Ref. 1). At that time, however, sulfur trioxide was made by the decomposition of sulfates. Phillips, in 1831 (Ref. 2), started a search for catalytic methods of oxidizing sulfur dioxide to sulfur trioxide by observing that the reaction could be effected by passing the reactants over "finely divided platinum, heated to a strong yellow heat." These observations served as the rudiments of the contact process of producing SO_3 through heterogeneous catalysis. Homogeneous catalysis for converting SO_2 to SO_3 is about a century older. The rudiments of the chamber process were known as early as 1740 (Ref. 3).

Despite the fact that these reactions were used both in the laboratory and in the commercial production of sulfuric acid for several hundred years, the importance of catalysis in the economics of these processes only began to be studied in detail in the twentieth Century. Therefore, the literature review for this program was limited to information published since 1900 on the catalytic oxidation of sulfur dioxide. Even though the community at large for several years has expressed concern about the air pollution problems resulting from the burning of fossil fuels, comparatively little appears in the literature concerning the application of technology to remove pollutants from flue gas. This being the case, all references in the literature dealing with the catalytic oxidation of sulfur dioxide to sulfur trioxide were reviewed.

The catalysts and promotors that seem most promising for gas-solid heterogeneous catalysis of SO_2 oxidation, on the basis of literature references, are listed in Table 1. Rhenium metal has also been reported as a possible catalyst for the oxidation of sulfur dioxide, but, until recently, has been too expensive to be economically feasible. Recent increased availability has forced the price of rhenium to the level of economic feasibility and its catalytic potential should be reevaluated (Ref. 4). Generally, the catalysts listed in Table are not effective below 400°C, although Mandelik (Ref. 5) claims 98% conversion in two stages "substantially below 400°C" with a vanadium pentoxide catalyst promoted with potash and phosphorus pentoxide. Bienstock (Ref. 6) reported tests with potash-promoted vanadium pentoxide in which 98% conversion of sulfur dioxide in flue gas (between 300° and 370°C) was claimed. However, from what has been seen to date, there appears to be no heterogeneous, gas-solid catalyst system which operates at temperatures below 300°C.

Table 1

CATALYSTS AND PROMOTERS FOR THE OXIDATION OF SULFUR DIOXIDE (HETEROGENEOUS CATALYSIS)

Catalyst	Promoters
V_2O_5	Bi_2O_3; alkali metal sulfates, oxides, and pyrosulfates; Ag_2SO_4, P_2O_5
Pt	Ag, Au, Ni, Pd
Iron, Iron oxides	CuO
Cr_2O_3	SnO_2, Al_2O_3, TiO_2, BaO
Carbon	-

Solid-liquid catalysis in sulfuric acid solution is a second type of heterogeneous catalysis operating at lower temperature. The SO_2 is absorbed in dilute sulfuric acid and catalytically oxidized while still in solution. Two catalysts are currently being used for this type of catalysis: selenium dioxide (Ref. 7), and manganese salts such as $MnSO_4$ (Ref. 8). In the course of the oxidation, the catalyst is reduced and must be reoxidized in a separate step. It might be argued that these processes are not truly catalytic, but they will be discussed herein for the sake of completeness.

All the catalytic processes that are homogeneous, gas-phase reactions are variations of the chamber process for the production of sulfuric acid, with nitrogen oxides acting as the oxidizing agents. Other types of catalysis which can operate at low temperatures are photo-oxidation, electrolysis, and oxidation in a spark discharge. Although Buff and Hoffman (Ref. 9) had oxidized SO_2 in a spark discharge as early as 1860, no commercially feasible methods employing high energy, light, or electric currents for catalyzing this reaction have actually been put into practice. A related type of homogeneous catalysis is effected by bombardment of the reactants with high energy particles such as photons, neutrons, x-rays, etc. These oxidative processes will also be considered in this report.

2. Factors Affecting Activity of Solid Catalysts

Since heterogeneous catalysis must of necessity involve reactions which occur on the surface of the catalyst, surface area is important in determining its activity. However, there are only certain portions of the total surface area of a catalyst which are able to adsorb the reactants and allow the reaction to occur. In other words, the total

surface of the catalyst contains areas of high catalytic activity, i.e., active sites. Two catalysts with equal surface areas, therefore, may have different activities resulting from a difference in the concentration of active sites on their surfaces. A related property of catalyst particles which affects activity is porosity.

The outer surface of a catalyst is the first surface poisoned, but it makes up only a fraction of the total surface area of a porous catalyst pellet. Therefore, it is often the inner surface area of the pore walls that determines catalyst efficiency. For extremely fast reactions, the diffusion of the reactants through the pores of the catalyst is the rate-determining step.

Another set of physical properties also thought to affect activity results from defects in crystal lattices which, in turn, tend to result in active sites on the catalyst surface. Several investigators have reported evidence of effects on catalyst properties of lattice imperfections such as dislocations and point defects (Ref. 10 through 14). Since there is a direct relationship between point defects in crystal lattice and the semiconductor properties of a crystal, it has been suggested that the semiconductor properties of catalysts could be used to predict their relative activities (Ref. 15). A good correlation, if one could actually be found, between semiconduction and catalytic activity would be a powerful tool in catalyst design. Thus far, no such correlation has been reported. The relationship of catalyst activity to crystal defects is intimately connected to the question of the effect of radiation on catalyst activity. The activation of catalysts by irradiation is universally felt to result from the creation (by the radiant energy) of lattice defects in catalyst crystals. However, on prolonged exposure to elevated temperatures, these defects tend to be "annealed" out with loss of the added activity.

Over thirty years ago Eyring (Ref. 16) and Horiuti (Ref. 17) calculated the magnitude of the activation energies of adsorption of hydrogen on various substates. They concluded from their studies that the lattice spacing would play a dominant role in determining the magnitude of the activation energy of adsorption. This work led to the concept that lattice spacing and the spatial arrangement of atoms in a catalyst crystal would affect the activity of the catalyst in a particular reaction. This is the basis of the so-called "geometric factor" as a parameter in determining catalytic activities. These effects are taken to result from the fact that the geometry of the species adsorbed on the catalyst surface fits with varying degrees of ease into the templates formed by the arrangement of atoms on that surface. The results of the simple case treated by Eyring and Horiuti, could be explained on the basis of lattice spacing, but the activities of more complicated catalyst systems are not easily predicted on the basis of the "geometric factor."

3. Comparison of Platinum and Vanadium as Catalysts

During the period of the development of vanadium catalysts in the United States (1927-30), attention was given to the following objections to the platinum catalysts then in use: (a) they were expensive, (b) they were extremely sensitive to poisons even in minute amounts, and (c) their conversion efficiencies were low. These same reasons are often given today to explain why the use of platinum catalysts has been completely supplanted in the contact process over the last three decades. However, we felt that it would be worthwhile to review these arguments and see if technological advances during that period would not have some effect on the validity of the arguments brought forth in support of the use of vanadium masses in this process. This seemed particularly necessary since we could find no published evaluation of the relative merits of these catalysts since the outbreak of World War II.

A number of papers were published in the early thirties comparing the catalytic properties of vanadium and platinum masses (Ref. 18-23). The state of the arguments as of 1936 was fairly accurately summarized by Farlie (Ref. 24) as follows:

I. Two Viewpoints of Comparison.

The two groups of catalysts may be compared from two different standpoints with regard to cost of catalyst, namely, (a) on the basis of manufracture; and (b) on the basis of manufacturing cost plus royalties.

II. Disadvantages Attributed to Vanadium.

1. Thompson (Ref. 18) making the comparison from standpoint "b", brought out that the prices charged for vanadium have been much too high, compared with the prices of platinum masses.

2. Thompson also emphasized the disadvantage of vanadium in that it handles only 7 to 8 percent SO_2 gas, as compared with 10 percent gas handled by platinum. Vanadium catalyst can handle 9 or 10 percent SO_2 gas, as has been demonstrated with Calco mass and on a laboratory scale with Selden mass; but in plant practice, the large majority of vanadium-mass plants actually do operate on gas within the range 6 to 8 percent SO_2.

3. Neumann (Ref. 19) and Streicher (Ref. 20) have pointed out the disadvantage of vanadium, as compared with platinum, in respect to overloading capacity.

4. Vanadium and platinum masses are affected unfavorably by accumulations of dust within the catalyst bed.

5. When worn out, vanadium mass has no salvage value.

III. Advantages Claimed for Vanadium

1. Vanadium maintains its conversion efficiency undiminished for a longer period than platinum.

2. The average conversion efficiency under normal loading is higher for vanadium than for platinum.

3. Vanadium catalysts are immune to "poisoning" by arsenic, chlorine, and some other elements which harmfully affect the activity of platinum masses. However, for the reasons set forth above, such immunity to poisoning has become of relatively slight importance.

4. On the basis of manufacture cost, vanadium is initially cheaper per daily ton of H_2SO_4 than platinum. However, when the salvage value of platinum is taken into account, this advantage is materially reduced. Also, with high royalty charges added to the cost of manufacturing vanadium mass, the advantage of lower initial cost of catalyst is yielded.

5. Vanadium mass offers less operative trouble and anxiety than platinum, especially when operating with metallurgical gases.

6. The latest vanadium masses are hard, rugged, and able to withstand handling without crumbling.

7. By means of vanadium mass, any country possessing supplies of vanadium among its natural resources is independent of foreign countries for raw material for the manufacture of sulfuric acid catalysts. This is a decided advantage in time of war.

IV. Disadvantages Attributed to Platinum

1. Platinum, even if not "poisoned", suffers a gradual decline in activity with use over a period of years, and at least (within 10 years) especially in the primary converter.

2. In a primary converter the platinum catalyst life is likely to be shorter than that of vanadium mass.

3. Platinized asbestos and magnesium sulfate are subject to "poisoning" by arsenic, chlorine, etc.

4. Platinized asbestos is fragile and liable to be damaged in handling or to be compacted in use.

5. As mentioned, both groups of catalysts become choked by deposits of dust within the bed.

V. Advantages Claimed for Platinum

1. Platinum can be reclaimed from a spent mass, to the extent of 90 percent of the weight originally introduced.

2. The price of platinum has fallen to 25 percent or less of its 1920 price.

3. The quantity of platinum in the modern platinized catalysts has been reduced to 2 or 3 troy ounces per daily ton of H_2SO_4 produced.

4. The manufacturing cost of modern platinum catalysts is in the neighborhood of $150 to $200 per daily ton of H_2SO_4, including the cost of the platinum, of which over 90 percent is later reclaimed.

5. Platinum catalysts have a much higher capacity for overloading at sustained conversion efficiency than vanadium masses.

6. In plant practice, platinum handles gas containing from 2 to 3 percent more SO_2 than the vanadium masses most widely employed. This means substantially larger production capacity and smaller power expense, for a given plant investment, with platinum catalysts.

7. Platinized silica gel is reported to be immune to arsenic poisoning.

8. According to U.S. Patent 1,384,566 with hot gas-purification, other platinum catalysts are not poisoned by either arsenic or sulfuric acid mist.

On the basis of the above arguments, Thompson, who published the most extensive article on the subject, concluded that platinum was the better of the two catalysts.

Since World War II, a great deal of progress has been made in technology. Therefore, it is worthwhile to reevaluate the platinum versus vanadium controversy in the light of these advances. First, the early platinum catalysts had surface areas of only several square meters per gram; today, platinum catalysts are produced with surface areas of 200 square meters per gram.

Further, vanadium catalysts in 1939 were being installed in only new plants while it was generally only the older plants which used platinum catalysts. It may be that some of the differences in the production figures obtained from these two types of installations resulted from better plant design rather than better catalyst mass.

The problem of the largest concentration of SO_2 that can be handled economically in the feed stream by the two types of masses might be an important consideration in the design of a manufacturing plant for H_2SO_4. However, in oxidizing flue gases of fixed lower level SO_2 concentration, this criterion is less meaningful.

4. Conversion of SO_2 Under Equilibrium Conditions

The degree of conversion of SO_2 to SO_3 under equilibrium conditions can be calculated by the procedure outlined by Dixon and Longfield (Ref. 25). These authors assume, however, that the SO_2 feed gas is produced by burning sulfur in air at two atmospheres pressure. In flue gas the equations representing the partial pressures of the components of interest are as follows:

$$P_{O_2} = \frac{[b-0.5a(1-y)]P_t}{1-0.5a(1-y)} \qquad (1)$$

$$P_{SO_2} = \frac{a \cdot y \cdot P_t}{1-0.5a(1-y)} \qquad (2)$$

$$P_{SO_3} = \frac{a(1-y)P_t}{1-0.5a(1-y)} \qquad (3)$$

where: P_t = total pressure of all flue gas components (atm.)

P_x = partial pressure of component x in flue gas (atm.)

a = initial fraction of SO_2 in flue gas

b = initial fraction of O_2 in flue gas

y = fraction of SO_2 remaining unconverted at equilibrium

The equilibrium constant of the reaction:

$$SO_2 + 1/2\ O_2 = SO_3$$

is given by equation 4.

$$K_p = \frac{P_{SO_3}}{P_{SO_2}\ (P_{O_2})^{1/2}} \qquad (4)$$

If we combine equations (1)thru (4) we obtain

$$0.5a[P_t \cdot K_p{}^2 - 1]y^3 + [P_t \cdot K_p{}^2(b-0.5a)-(1-1.5a)]y^2 + [2-1.5a]y + [-1+0.5a] = 0 \qquad (5)$$

The cubic equation (5) can be solved for y and for a range of values of a, b, P_t and K_p. Only values of y between zero and one will have physical meaning. These y values can then be substituted into equations 1, 2, and 3 to give values of P_{O_2}, P_{SO_2}. and P_{SO_3}. The fraction of SO_2 converted is of course $1 - y$. The values of K_p used in solving these equations were calculated from the following equation given by Dixon and Longfield (Ref. 25).

$$\log K_p = \frac{4,956}{RT} - \frac{4.678}{R} \qquad (6)$$

where: T = temperature (°K)

R = gas constant

The calculated equilibrium conversion versus temperature is plotted in Figure 1 for a flue gas containing 0.3 mole percent SO_2 and several different concentrations of O_2.

The equilibrium conversion values start to drop below 100% for temperatures of ~750°K (477°C) or higher. At each temperature, the presence of more initial oxygen results in higher values of the equilibrium conversion. Similar computer calculations were made for different initial concentrations of SO_2. For example, at 2.5 vol of O_2, initial, the equilibrium conversion values were computed at 650°, 800°, and 900°K, respectively, and are shown in Table 2. Details of the calculations are shown in Appendix I.

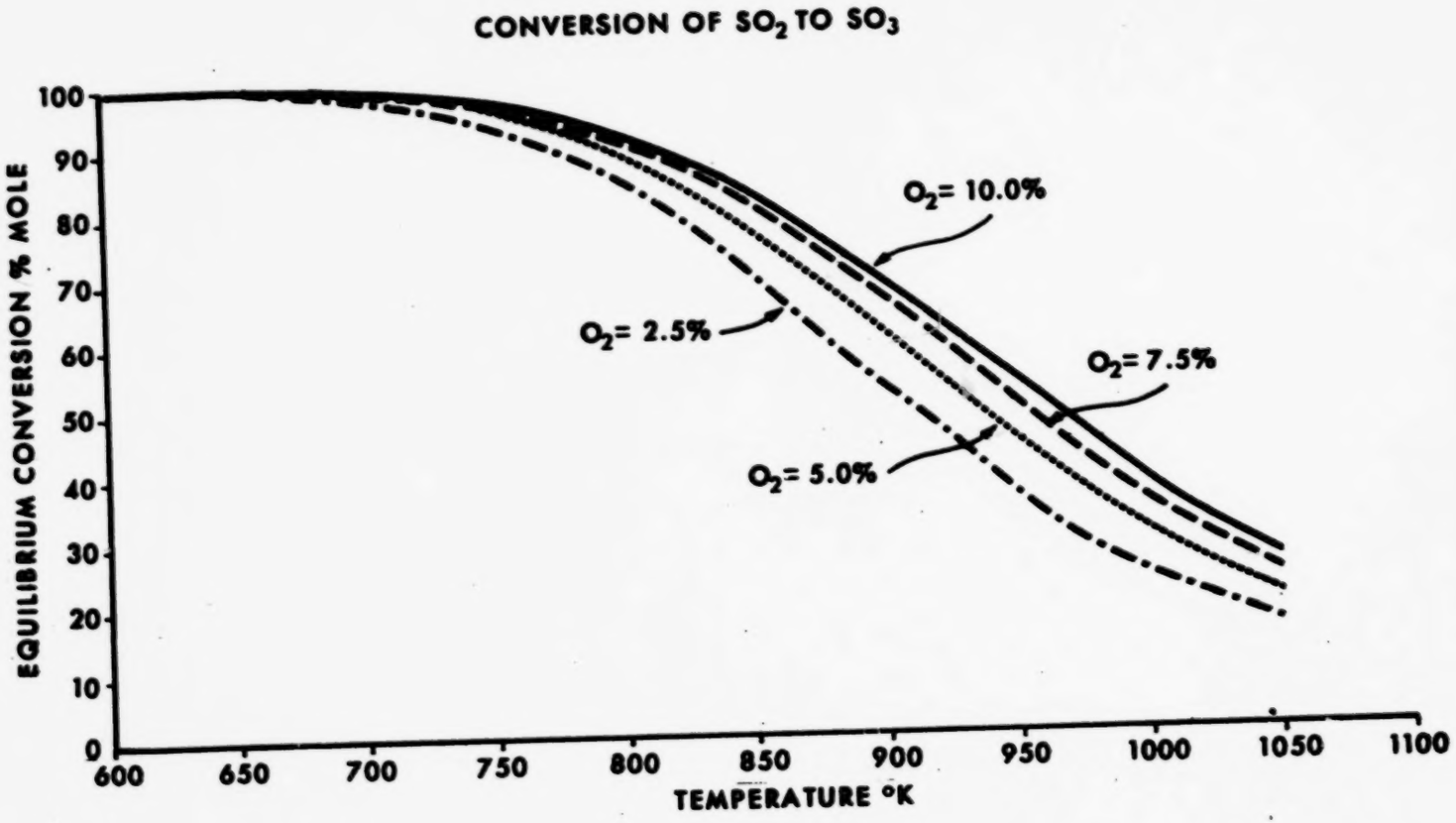

Figure 1. Computed Equilibrium Conversion Values

Table 2

COMPUTED EQUILIBRIUM CONVERSION VALUES FOR: $SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$

SO_2 Initial Vol. %	Temperature, °K 650	800	900
0.1	0.993	0.844	0.525
0.2	0.994	0.843	0.523
0.3	0.994	0.842	0.521
0.4	0.995	0.842	0.518
0.5	0.995	0.842	0.516
0.6	0.996	0.842	0.513

Below 800°K, the changes in equilibrium conversion values are insignificant in view of the accuracy inherent to the computer evaluation. At 900°K, the equilibrium conversion value drops with increasing initial concentration of SO_2 in the flue gas feed. This agrees with a statement in (Ref. 26):

> "Increasing the SO_2 content of the feed results in a lower equilibrium oxygen concentration and a lower equilibrium conversion of SO_2 to SO_3 at any given temperature."

It is realized that these calculated equilibrium conversion factors are of limited value for two reasons: (1) the desirable temperature range for operation is below 900°K, a temperature range at which the equilibrium conversion factor is close to 100%, and (2) the short residence times in a practical reactor for flue gas treatment preclude the attainment of equilibrium conditions.

5. Conversion of SO_2 Under Non-Equilibrium Conditions

a. Introduction

The primary objective in this phase of the search was to obtain kinetic data on the catalytic oxidation of SO_2 under flue gas conditions, that is, very low concentrations of SO_2 and O_2, compared to the usual concentrations of these gases in gas mixtures processed with the contact method for producing sulfuric acid. It was realized, even before this program started, that not much literature was available pertinent to the primary objective. A secondary objective, then, was to assess the literature on catalytic oxidation under contact process conditions (8-10% SO_2, 20% O_2). This assessment would consist of a critical study of the kinetic models and kinetic data presented in various papers on the subject.

To achieve this goal, a wide variety of kinetic equations appearing in the literature (Ref. 27-44) were analyzed and are discussed in some detail in subsequent sections in this volume.

b. Oxidation over Vanadium Catalysts

Napier et al., (Ref. 27) discusses the results of a preliminary study of the catalytic oxidation of SO_2 under flue gas conditions. The basic composition (by volume) of the gas mixture was:

CO_2 = 13.5%, O_2 = 4.7%, N_2 = 76.3%, H_2O = 5.4% and SO_2 = 0.1%

An industrial vanadium catalyst was used. The catalyst contained V_2O_5 and K_2SO_4 with a silica support and ranged in composition from 6.5-7.5 weight percent V_2O_5 and 6.3-10.6 weight percent K_2O. The authors found that one of these catalysts (6.7% V_2O_5, 9.5% K_2O) yielded a fractional conversion of 93% at 429°C and of 82% at 511°C. Conversion was found to be independent of contact time, in the range studied, as shown in Table

Table 3

EFFECT OF CONTACT TIME ON CONVERSION

Weight of Catalyst, g	Contact Time, Sec.	Fractional Conversion, %
3.1	0.43	94
2.0	0.27	94
1.4	0.19	98
0.6	0.09	94

A limited amount of work at other concentrations of SO_2 and O_2 showed that varying the SO_2 concentration over the range 0.34% - 0.27% (by volume) did not produce any large changes in the fractional conversion. The fractional conversion was consistently over 90%. The variation of conversion with oxygen content was studied at two additional oxygen concentrations: 6.8 vol % and 1.85 vol. % O_2. The fractional conversions obtained were equal for all practical purposes, i.e., 90% or better.

The main value of this exploratory work is, to quote Napier,

> "firstly, to confirm that the presence of water vapor and carbon dioxide in the gases has no adverse effect on the catalyst, and secondly to show that the required contact time at low sulphur dioxide concentration is much lower than that used in the contact process"..... and (it) suggests that it might be technically feasible to oxidize sulphur dioxide in boiler flue gases."

In the main approach to the problem of kinetics of oxidation of SO_2 over V_2O_5 and of obtaining a rate equation, two general methods have been followed. First is the empirical method. This method involves assuming that the rate is given by

$$r = k\, f\,(P_{SO_2}, P_{O_2}, P_{SO_3})$$

and then by fitting the rate with assumed forms of the function

$$f(P_{SO_2}, P_{O_2}, P_{SO_2})$$

one obtains a rate equation. Various forms have been chosen for the function f as shown in Table 4. These rate laws usually hold for certain conversion ranges and temperatures. Most were not purported to hold through wide ranges of conversion of SO_2 to SO_3. Other equations were reported that were supposed to hold through wide ranges of conversion. Some of these are shown in Table 5.
and were used in calculations described later. The catalysts used to obtain the kinetic data which were fit to these equations are listed in Table 6.

The second method employed the application of the "Theories Method" of Hougen and Watson (Ref. 45). These theories assume that gas-solid catalytic reactions take place by the following steps:

1. Diffusion of the gaseous reactants in the gas phase to the catalyst surface.

2. Adsorption of the reactants upon the surface.

3. Reaction between the adsorbed reactants on the surface.

4. Desorption of the products.

Table 4

FORMS USED FOR THE FUNCTION $f(P_{O_2}, P_{SO_2}, P_{SO_3})$

Author and Reference		
A. Boreskov (36)	$\left[\frac{P_{SO_2} - P_{SO_2}\ (eq.)}{P_{SO_3}^{1/2}}\right]$	
B. Boreskov (37)	$\frac{P_{SO_2}}{P_{SO_3}^{1/4}}$	
C. Boreskov (38)	$P_{O_2}\left(\frac{P_{SO_2}}{P_{SO_3}}\right)^{0.8}$	
D. Calderbank (34)	$P_{O_2}^{m}\ P_{SO_2}^{n}$	$0.72 < m < 0.85$ $0.35 < n < 0.43$
E. Zakerevski & Chang (41)	$P_{O_2}^{m}\ P_{SO_2}^{n}$	$n = 0.3$ $0.4 < m < 1.0$
F. Davidson-Thodos (43)	$P_{O_2}^{m}\ P_{SO_2}^{n}$	$-0.50 < m < 0$ $0.617 < n < 0.87$
	m and n depend on temperature between 643°F and 722°F as above. m increases and n decreases with T.	
G. Krichevskaya (46)	$P_{SO_2}^{1/2}\ P_{O_2}^{1/2}$	
H. Boreskov (44)	$\frac{P_{SO_2}\ P_{SO_2}}{P_{SO_2} + 0.7\ P_{SO_3}}\left[1 - \left(\frac{P_{SO_3}}{P_{SO_2}\ P_{O_2}\ K_p}\right)^2\right]$	

Table 5

LIST OF RATE EQUATIONS USED IN CALCULATIONS*

A. P. H. Calderbank

$$V = k\, P_{O_2}\, P_{SO_2}^{1/2} \left[1 - \frac{P_{SO_3}}{P_{SO_2}\, P_{O_2}^{1/2}\, K_p} \right]$$

$$\ln k = -\frac{31000}{RT} + 12.07$$

Applicable temperature range 370° - 500°C

B. R. B. Eklund

$$V = k\, P_{O_2} \left(\frac{P_{SO_2}}{P_{SO_3}} \right)^{1/2} \left[1 - \left(\frac{P_{SO_3}}{P_{SO_2}\, P_{O_2}^{1/2}\, K_p} \right) \right]^2$$

values of k obtained from table of Eklund:

T(°C)	500°	460	420	483
k(x10⁶)	27.0	10.3	2.0	19.0

Applicable temperature range 420-550°C

C. Mars and Maessen

$$V = kKP_{SO_2}\, P_{O_2} \left(\frac{1}{\sqrt{P_{SO_3}} + \sqrt{KP_{SO_2}}} \right)^2$$

$$K = 2.3 \times 10^{-8} \exp\left(\frac{27,200}{RT} \right)$$

*All rates above are in moles SO_2 per second per gram of catalyst and all pressures are in atmospheres. In all equations the value of K_p, the equilibrium constant for the gaseous reaction $SO_2 + 1/2\, O_2 \rightarrow SO_3$ is given by

$$\ln K_p = \frac{22,600}{RT} - \frac{21.36}{R}$$

Table 5 cont'd

for catalyst 1:

$$\ln k = \frac{-26,000}{RT} + \frac{15.89}{R}$$

for catalyst 3:

$$\ln k = \frac{-21,000}{RT} + \frac{10.89}{R}$$

Applicable temperature range: 400-500°C

D. Davidson-Thodos**

$$V = \left[\frac{\frac{k}{3600} P_{SO_2} P_{O_2}^{1/2} \left[1 - \left(\frac{P_{SO_3}}{P_{SO_2} P_{O_2}^{1/2} K_p} \right) \right]}{(1 + K_{SO_2} P_{SO_2} + \sqrt{K_{O_2} P_{O_2}} + K_{SO_3} P_{SO_3} + K_{N_2} P_{N_2})^2} \right]$$

$$\ln k = \frac{44,900}{RT} - \frac{34.51}{R}$$

$$\ln K_{SO_2} = \frac{50,400}{RT} - \frac{39.42}{R}$$

$$\ln \sqrt{K_{O_2}} = \frac{57,750}{RT} - \frac{46.6}{R}$$

$$\ln K_{SO_3} = -\frac{44,400}{RT} + \frac{44.13}{R}$$

$$\ln K_{N_2} = -\frac{36,350}{RT} + \frac{29.77}{R}$$

Applicable Temperature range: 340°-384°C

**The factor 1/3600 is used to convert the rate as given to moles SO_2 per second per gram. The temperature here is in °Rankine and R is in Btu/degree-mole.

Table 5 cont'd

E. <u>Goldman</u>

$$V = \left[\frac{k\, P_{SO_2}\, P_{SO_2}^{1/2} \left(1 - \frac{P_{SO_3}}{P_{SO_2}\, P_{O_2}^{1/2}\, K_p} \right)}{(1 + \sqrt{K_{O_2}\, P_{O_2}} + K_{SO_2}\, P_{SO_2} + K_{SO_3}\, P_{SO_3})^2} \right]$$

$$\ln k = \frac{15{,}709}{RT} - \frac{15.72}{R}$$

$$\ln K_{O_2} = \frac{28{,}769}{RT} - \frac{27.82}{R}$$

$$\ln K_{SO_2} = \frac{19.184}{RT} - \frac{20.58}{R}$$

$$\ln K_{SO_3} = \frac{43{,}493}{RT} - \frac{54.82}{R}$$

Applicable temperature range: 374-433°C

Table 6

CATALYSTS USED TO OBTAIN RATE EQUATIONS IN TABLE 5

Equation	Cat. Size	Catalyst Composition
1. P. H. Calderbank	10-14 mesh	V_2O_5 11.3%; K O; Other 4.6% Na Prepared by method given in Maxted, E.B., "Catalysis and Its Industrial Applications," p. 247 (London; Churchill) (1933)
2. R. B. Eklund	0.67-1.38 mm	Commercial catalyst - no analysis given
3. Mars & Maessen	0.5 mm	8.2% V_2O_5; 17% K; 5.1% Ca; 0.9% Na
Catalyst #1		The (K+Na)/V (atom/atom) is 2.8
Catalyst #3	0.5 mm	6.8% V_2O_5; 10% K; 0.7% Ca; 2.9% Na
		The (K+Na)/V atom/atom) is 2.5
4. Davidson-Thodos	3/16 in. spheres	~8% V_2O_5; 10% K_2O; 0.5% Fe
5. Goldman	60-80 mesh	Commercial catalyst - Davison Chemical Co., Code 902

Assuming that one step is rate controlling, Hougen and Watson derived rate equations for various type reactions. Various workers have fit SO_2 oxidation rate data to the equation that assumes the surface reaction is rate controlling. Equations D and E in Table 5 were arrived at by this method. In one of these (E), it is assumed that N_2 in the stream has no effect; in another (D), the nitrogen is included. The reason for considering N_2 is that it may compete with SO_2 and O_2 for adsorption sites. The term in brackets in D and E in Table 5 supposedly takes account of the reverse reaction of SO_3 decomposition. This term also appears in other equations that are arrived at by a more empirical approach than the Hougen-Watson approach.

It is obvious from Tables 4 and 5 that no accord seems to exist in the explanation of the rates of catalytic SO_2 oxidation for H_2SO_4 production (Ref. 27, 31, and 44).

The most recently published rate-law equation for SO_2 oxidation is that of Mars and Maessen (Ref. 28 and 29). They have shown that it is possible to fit the data of Eklund (Ref. 31) and of Boreskov (Ref. 44) to their kinetic equation (see Equation C, Table 5). This is a step in the right direction.

The basic assumption of Mars and Maessen is that, in the catalytic system, the following equilibrium is established continuously and instantaneously:

$$SO_2 + 2V^{+5} + O^{-2} \rightleftarrows SO_3 + 2V^{+4} \qquad (7)$$

This reaction is assumed to be a two phase equilibrium between the gas phase and the "solid" phase. The V^{+5}, V^{+4} and O^{-2} are believed to be dissolved in a thin liquid film on the surface of the catalyst. This liquid film is believed to be composed of melted alkali or alkaline earth pyrosulfates. Tandy (Ref. 47) has presented evidence that this melt actually does exist for alkali-promoted catalysts in the temperature range (400°-500°C) studied by Mars and Maessen.

The equation above is assumed to have an equilibrium constant:

$$K = \frac{(a_{V^{+4}})^2 \; P_{SO_3}}{(a_{V^{+5}})^2 \; P_{SO_2} a_{O^{-2}}} \qquad (8)$$

where a = activity coefficient

It is assumed that the activity coefficients of V^{+4} and V^{+5} are equal and that $a_{O^{-2}}$ is constant so that it may be incorporated into K to give the equilibrium constant:

$$K = \frac{[V^{+4}]^2 \; P_{SO_3}}{[V^{+5}]^2 \; P_{SO_2}} \qquad (9)$$

The rate of reaction is controlled by the rate of oxidation of V^{+4} to V^{+5} by O_2 in the gas phase as follows:

$$O_2 + V^{+4} = V^{+5} + O_2^-$$

and the rate equation of the forward reaction is given by:

$$V = k \; P_{O_2} \; [V^{+4}]^m \qquad (10)$$

Using (9) and (10), it is possible to show that the rate is:

$$r = k \; P_{O_2} \left[\frac{\sqrt{K \; P_{SO_2}}}{\sqrt{P_{SO_3}} + \sqrt{KP_{SO_2}}} \right]^m \qquad (11)$$

The best fit of the rate data indicates that the value of m is near 2 so that m = 2 is chosen. Equation (11) is the same then as Equation (C), Table

The contention of Mars and Maessen that equilibrium [Eq. (7)] is rapidly established may be true, but, from their discussion of their experiments, it seems that one can only say that equilibrium is established but not how rapidly it is established. The question of how rapidly it is established may not be very important, since a steady state condition may explain the situation just as well.

The assumption that equilibrium exists is reasonable because the equilibrium constant can be directly determined and calculated from kinetic data to obtain fair agreement. Further the fact that their

equation fits the data of two other investigators lends support to their treatment.

Kadlec and Regner (Ref. 147-149) report that their kinetic data support the assumption of Mars and Maesson that the oxidation of V^{+4} is the rate-determining step, but they picture this process as happening in the three steps given below:

(a) $O_2 + V^{+4} \rightleftarrows V^{+5} + O_2^-$

(b) $O_2^- + V^{+4} \rightleftarrows V^{+5} + 2\ O^-$

(c) $O^- + V^{+4} \rightleftarrows V^{+5} + O^{-2}$

They feel that, consistent with their data, (b) is the rate-controlling step.

Of Equation (C) in Table 5 is algebraically manipulated, it can be written in the form.

$$\left(\frac{P_{O_2}}{V}\right)^{1/2} = \left(\frac{1}{k}\right)^{1/2} + \left(\frac{1}{kK}\right)^{1/2}\left(\frac{P_{SO_3}}{P_{SO_2}}\right)^{1/2} \qquad (12)$$

A graph of $(P_{O_2}/V)^{1/2}$ versus $(P_{SO_3}/P_{SO_2})^{1/2}$ should yield a straight line.

The results of this operation for Mars and Maessen's data, Eklund's data, and Boreskov's data are shown in Figures 2-5 taken from Reference 29. These graphs indicate that Equation (12) predicts the data reasonably well for higher temperature but that some deviations are observed at lower temperatures. How low a temperature is needed seems to depend upon the particular catalyst used. Boreskov's data are at 485°C only, so temperature comparison is not valid in this case. It should be noted that the lines obtained by plotting data according to Equation (12) are almost parallel for different temperatures in the high temperature range. This indicates that the expression $(1/kK)^{1/2}$ is almost independent of temperature. This is seen to be approximately true from the expressions for K and k of Equation (C) in Table 5. At lower temperatures, this term changes with temperature and the lines at lower temperatures have different slopes than for higher temperatures. They also have a curvature that appears to depend on the P_{SO_3}/P_{SO_2} ratio.

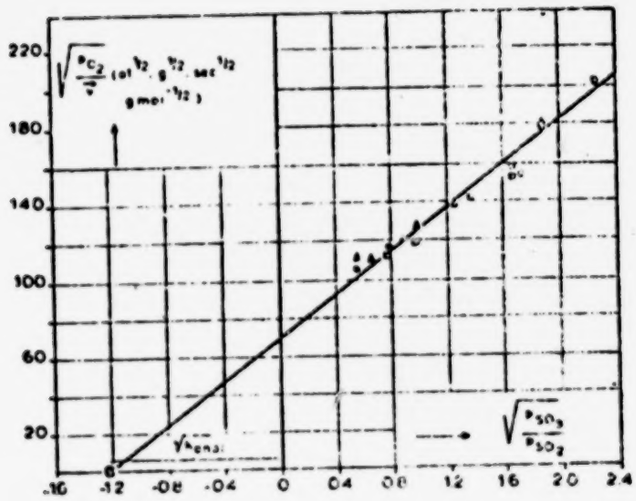

Figure 2. Results of Experiments of Boreskov, et al

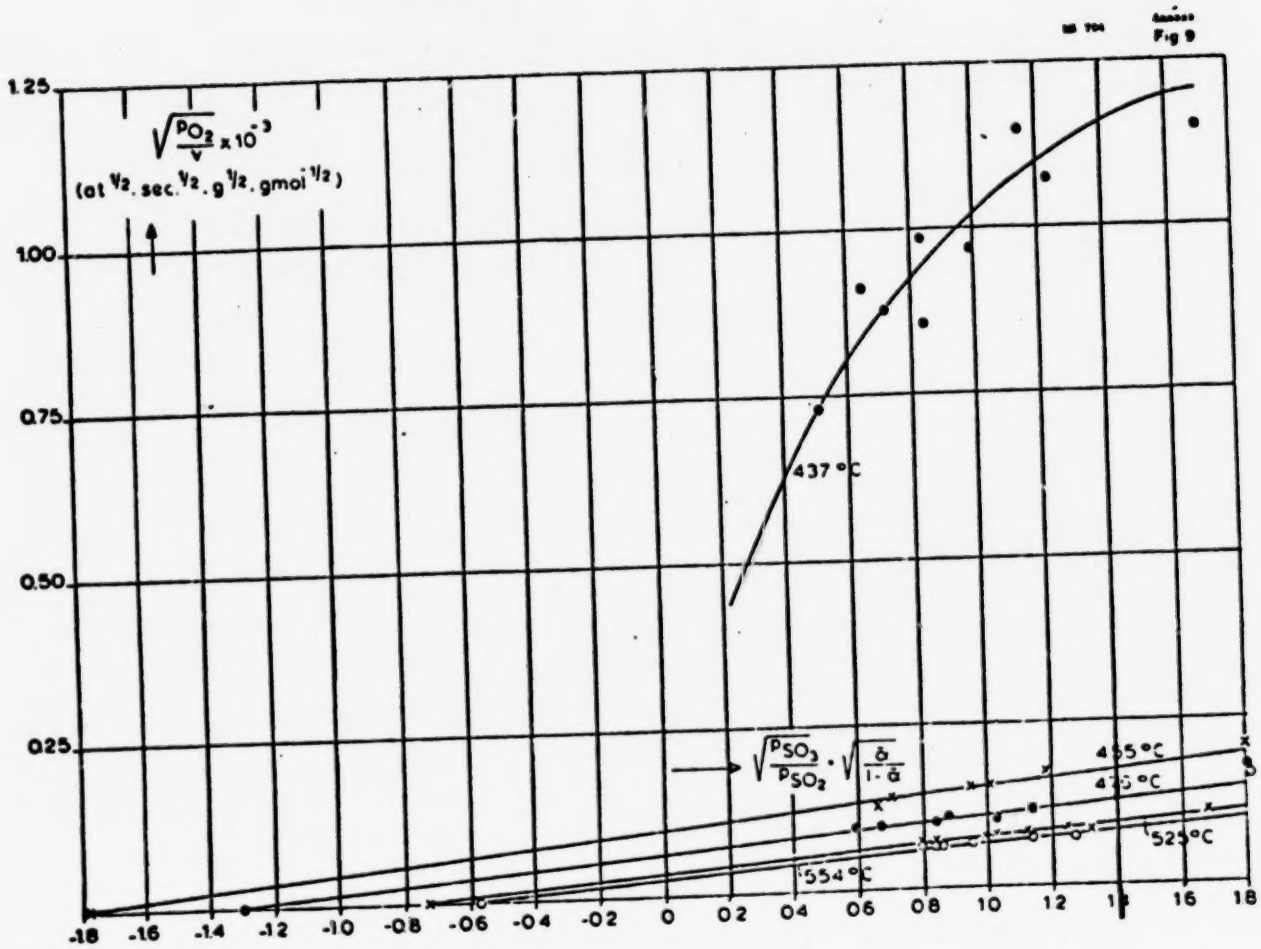

Figure 3. Results of Eklund's Measurements

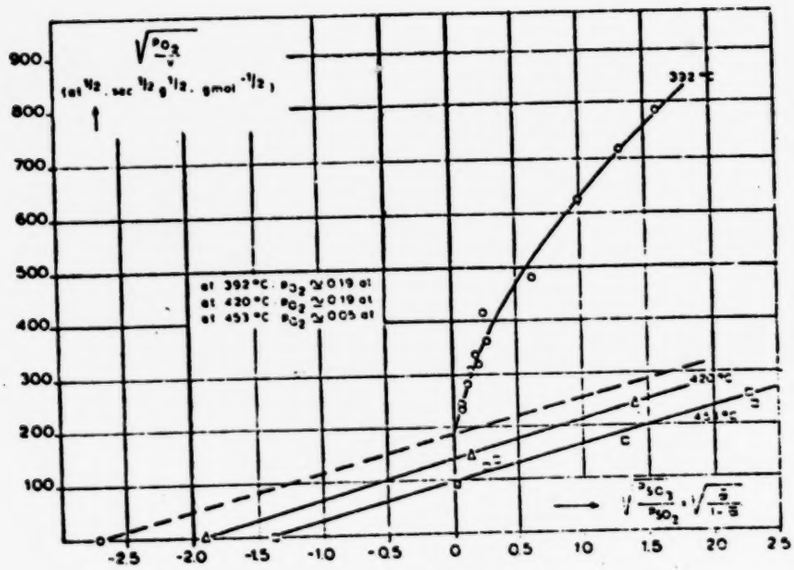

Figure 4. Results of Kinetic Measurements on Catalyst 3

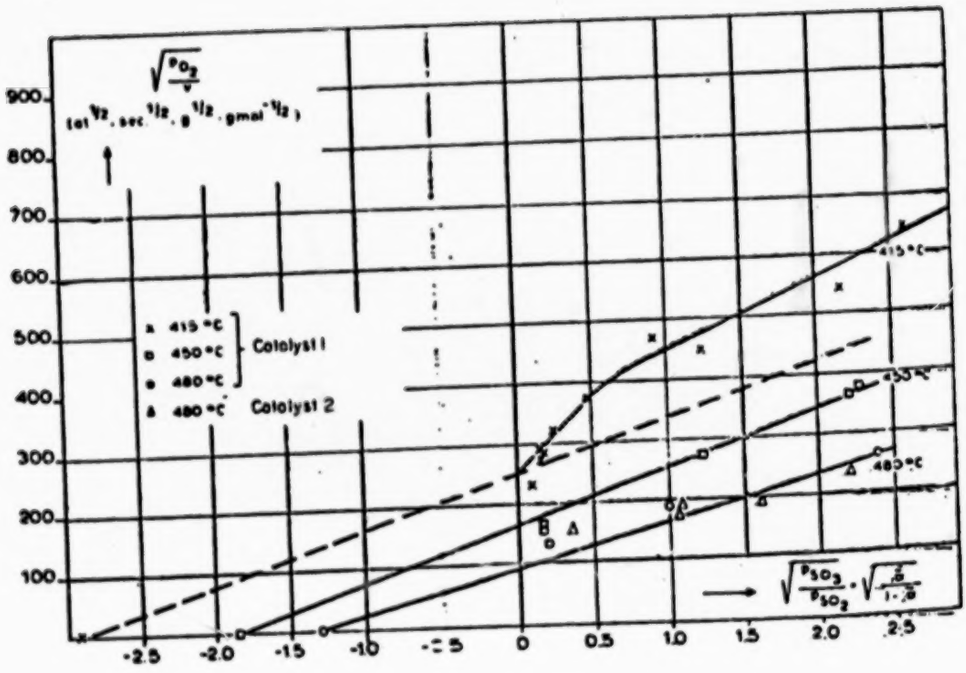

Figure 5. Results of Kinetic Measurements on Catalyst 1 and 2

The Mars and Maessen equation will not be valid when one approaches equilibrium for the reaction $SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$ because no provision is made for the rate to approach zero as equilibrium is approached. Their graphs, however, indicate validity of their equation up to about 85% conversion.

Several investigators (Ref. 28, 44) have reported that if one plots the logarithm of the specific rate constant, or of the rate itself, versus reciprocal temperature, two straight lines of different slope occur in different temperature ranges. The break in the Arrhenius plot occurs between 400°C and 500°C and seems to depend on the composition of the gas phase and the catalyst used.

The break in the curve indicates a probable change in mechanism. This could be explained by the fact that between 400-500°C, the pyrosulfate melt forms and that the mechanism of catalysis is different above the melting point than below the melting point. This melting point may be affected by the amount of V^{+4} (as $VOSO_4$) present which is determined by the gas composition according to Equation (7). Mars and Maessen, in a 1964 publication (Ref. 28), seemed to agree with the existence of a break in the curve, but, in their latest paper (Ref. 29), they are not as sure and indicate that their rate equation and data do not predict a break in the Arrhenius plot. However, the fact that some deviation from their equation at lower temperatures exists would indicate that the possibility of a break in the Arrhenius graph is high. Their data is consistent with the change in mechanism occurring by a phase change on the outer surface of the catalyst. For a solid outer surface, the equilibrium in Equation (7) above may not exist or the assumptions leading to Equation (9) may not be valid and so the derivation of Mars and Maessen equation may not be valid. The break in the Arrhenius graph is further supported by data from Calderbank (Ref. 34) who studied the adsorption equilibrium of O_2 and SO_2 on a K_2SO_4 promoted V_2O_5 catalyst. He found that between 400°-500°C the type of active centers occupied by the adsorbed molecules on the catalyst surface changed. The point of change depended, for a given temperature, on the pressure of O_2 or SO_2 (whichever was being adsorbed). A change in the type of adsorption centers could cause a change in mechanism and consequently a change in rate. Calderbank found that O_2 (ΔH_{ads} = 6.4 kcal/mole) is much less strongly chemisorbed than SO_2 (ΔH_{ads} = 28.8 kcal/mole). He also studied the rates of adsorption of SO_2 and O_2 on the catalyst surface but, due to their magnitude, did this at lower temperatures (250-300°C) than those at which the equilibrium adsorption and SO_2 oxidation are done (400-500°C). From these, he concludes that the mechanism for oxidation is:

(a) $SO_2 + 2e(surface) \rightarrow SO_2^{--}$ (fast chemisorption) (13)

(b) $SO_2^{--} + O_2 \rightarrow SO_3 + O^{--}$ (slow second-order reaction between gaseous O_2 and adsorbed SO_2) (14)

(c) $O^{--} \rightarrow 1/2\ O_2 + 2e(surface)$ (fast desorption) (15)

(d) $SO_3(surface) \rightarrow SO_3(gaseous)$ (fast desorption) (16)

He chose reaction (14) as the slow reaction so that the rate is:

$$V = k' P_{O_2}{}^{a_{SO_2}} \qquad (17)$$

and fits the data best to:

$$a_{SO_2} = k'' P_{SO_2}{}^{0.4} \qquad (18)$$

so that

$$V = k P_{SO_2}{}^{0.4} P_{O_2} \qquad (19)$$

where $k = k'k''$

This equation holds only for low conversions (<15%). In a later paper (Ref. 48), Calderbank expands Equation (19) to fit cases for high percent conversions by taking account of the decomposition of SO_3. He did this by choosing the exponent of P_{SO_2} as 0.5 above instead of 0.4 (which he justified by saying it is sufficient for design purposes). He then wrote the rate as:

$$V = k_1 P_{SO_2} P_{O_2} - k_2 f (P_{SO_2}, P_{O_2}, P_{SO_3}) \qquad (20)$$

and chose the function f so that V = 0 at equilibrium and $k_1/k_2 = K_p$. This gave Equation (A) in Table

Of the remaining equations in Table used in the calculation described below, two of them (D and E) are derived from Hougen-Watson theory assuming that the rate of reaction between surface adsorbed SO_2 and O_2 is the rate-controlling step. The main difference in these two equations is that one theorizes that N_2 competes for the

active site (D, Davidson-Thodos) while the other does not (E, Goldman, et al). Since Calderbank (Ref. 34) found that N_2 is not adsorbed by the catalyst he used at the temperature above 400°C, it seems that Equation (E) in Table is basically more correct than Equation (D). This is in addition to the fact that Equation (D) predicts a decrease in rate with increase in temperature, an unlikely situation. The investigation by Goldman, et al (Ref. 30) also studied the relative effects of fluidized and fixed beds on the rate. They fitted both sets of data to the same rate equation but found that the rate was 3-4 times higher with fluidized beds than for fixed beds. Both Goldman, et al, and Davidson and Thodos used total pressures of over one atmosphere; these did not exceed 1.5 stmosphere for Davidson-Thodos and 2.5 atmosphere for Goldman, et al. Since all rate equations are in partial pressures of reactants, this is probably not critical for these small differences. Equation (B) in Table was proposed by Eklund (Ref. 31) and was arrived at semi-empirically. The Hougen-Watson theory influenced his derivation but was modified to fit the experimental data. He found that the value of the specific rate constant may vary slightly with the catalyst size. The value used is for commercial-sized catalyst pellets, which are cylinders approximately 1/3 inch in diameter by 1 inch long.

The form (H) in Table 4 is used by Boreskov (Ref. 36, 44) and is supposed to be valid over wide conversion ranges.

A general theme of most of the papers on oxidation kinetics is that the data is not presented in its entirety in table form, thus preventing the reader from using it if desired. Usually graphs of the data are drawn but, in the case of Boreskov and others, the graphs are not large enough for reading and are incompletely labeled.

The present state of catalytic oxidation of SO_2 seems to be the following:

> V_2O_5 catalysts promoted with alkali metal compounds are the most popular and active catalysts, K being the most commonly used promoter for economic reasons. The reaction is believed to take place, at least partly, in a liquid phase of pyrosulfates on the surface in which the V_2O_5 dissolves. The V^{+5} is at least partly reduced to V^{+4} in the reaction, and the relative amounts appear to depend on the relative amounts of SO_3 and SO_2 in the gas contacting the catalyst, the temperature, and which and how much promoter is used.

There appears to be a change in mechanisms of catalysts between 400-500°C which probably is related to the phase changes of the pyrosulfate promoter. The relationships between these phenomena are not known and most work has been done for SO_2 concentrations between 4% and 15% by volume.

The rate equations in Table 5 are purported to be valid for high conversions and the relevant constants were available. These rate equations were used to calculate conversion of SO_2 as a function of time and also as a function of W/F, where W is the weight of catalyst required for a given conversion and F is the flow rate in moles of SO_2 per second. The calculations were performed with a computer and are discussed in Appendix II.

The calculations were made at flue gas conditions

$$(P_{O_2} = 0.028 \text{ atm}, P_{SO_2} = 0.003 \text{ atm and } P_{N_2} = \text{atm initially})$$

for the purpose of comparing the various equations in regard to their predictions about contact time and W/F values. Calculations were made at temperatures from 375° to 500°C. None of the equations were valid over the whole temperature range; however, in some cases the equation was assumed to be valid outside the reported range by 25°C or so.

In AppendixII, Figures 1 through 7 show the percent conversion of SO_2 versus contact time at various temperatures as calculated using the various rate equations. Figures 8 through 14 show the percent conversion of SO_2 versus W/F.

It is seen in the graphs that the two catalysts for Mars and Maessen and Eklund's data give curves that group more closely together. This is expected since Mars and Maessen fitted Eklund's data to their equation. If calculations could have been made with Boreskov's equation, it should also be near the values given by Mars and Maessen, and Eklund's equations.

c. Oxidation Over Platinum Catalyst

A list of the equations that have been used historically to fit kinetic data for SO_2 oxidation over a platinum catalyst are given in Table 7.

Lewis and Ries (Ref. 49) tried to fit Equations (A) and (B) in Table 7 to experimental data that they generated on the rate of oxidation of sulfur dioxide over platinum under a variety of conditions. They reported three types of experiments. In the first, SO_2 was oxidized in air. Both the temperature and concentration were varied in these experiments, the temperature from 400°C to 450°C, and the initial concentration of SO_2 from 0.109 to 0.519 mole percent.

In the second type of experiment, the sulfur dioxide was present at about the same concentration as in the first type, but the concentration of oxygen was reduced by dilution with nitrogen. The temperature was maintained at 450°C.

The third type of experiment employed gas mixtures consisting of 0.5 mole percent or less of SO_2, 1 to 5 mole percent of SO_3, and the remainder oxygen and nitrogen.

Lewis and Ries concluded that kinetic Equation (A) in Table 7 fit their data and the data reported earlier by Knietsch (Ref. 50). They also concluded that their Equation (A) could be made to fit the data more accurately than could Bodenstein's (Ref. 51) or an equation derived from the law of mass action. Unfortunately, no attempt was made by Lewis and Ries to determine the reaction constant and thus the rate of reaction in some sort of standard units, such as moles converted per second per gram of catalyst. In fact, during their experiments, they did not determine the weight of catalyst in the reactor.

Roiter and co-workers (Ref. 52) investigated the oxidation of SO_2 over platinum catalyst under equilibrium and non-equilibrium conditions by use of radioactive $S^{35}O_2$. They were able to fit their data to Equation (A), and, on the basis of the fit, proposed two alternative mechanisms for this reaction:

Table 7

RATE EQUATIONS FOR THE OXIDATION OF SO_2 OVER PLATINUM CATALYST

A. Lewis and Ries (Ref.49)

$$\frac{-dm}{dt} = kP_{SO_2}\left[\ln\left(\frac{P_{SO_3}}{P_{SO_2}}\right)^e - \ln\frac{P_{SO_3}}{P_{SO_2}}\right]$$

M = moles of SO_2

P_x = partial pressure of component x (atm)

k = constant

Superscript 'e' denotes equilibrium conditions

B. Bodenstein (Ref.51)

$$\frac{dc}{dt} = k\frac{P_{SO_2}}{(P_{SO_3})^{1/2}}$$

c = concentration of SO_2 (moles/cc)

C. Roiter, et al. (Ref.52)

$$\frac{dm}{dt} = k\left[P_{O_2}^{.5}\ P_{SO_2} - \frac{P_{SO_3}}{K_e}\right]$$

K_e = equilibrium constant

D. Uyehara and Watson (Ref.53)

$$V = \frac{k_1}{(1 + \sqrt{P_{O_2}}\ \sqrt{K_{O_2}} + P_{SO_3}\ K_{SO_3})^2} \cdot \left(P_{O_2}^{.5}\ P_{SO_2} - \frac{P_{SO_3}}{K_e}\right)$$

R = Gas constant (cal/mole-°K)

V = reaction rate (moles SO_3 produced/sec - g of catalyst)

k = 2.77×10^{-4} (-8000/T + 14.154)

K_{O_2} = $e^{(20,360/RT-23.0/R)}$

K_{SO_3} = $e^{(16,800/RT-17.51/R)}$

I		II	
(a)	$O_2 \rightleftharpoons 2\,O$	(a)	$SO_2 + O_2 \rightleftharpoons SO_3 + O$
(b)	$O + SO_2 \rightleftharpoons SO_3$	(b)	$O + SO_2 \rightleftharpoons SO_3$
		(c)	$2\,O \rightleftharpoons O_2$

In each case, reaction (b) was considered as the rate-determining step. They were unable to distinguish between the two mechanisms, using their data. To do this they would have had to make a detailed investigation of the relationship between reaction rate and oxygen concentration.

All of the experiments in this study by Roiter, et al were performed with the concentrations of sulfur dioxide and oxygen appropriate for a contact sulfuric acid plant. When their expressions are applied to the oxidation of SO_2 under flue gas conditions, the contact times predicted to obtain 90% conversion of the SO_2 are an order of magnitude too high compared to laboratory test data generated on this program.

A modification of the reaction constants is afforded by the equation of Uyehara and Watson (Ref.53), (see equations C and D in Table 7). The k of the Roiter equation is replaced by a more complicated expression that varies not only with temperature but also with the chemical composition of the reaction mixture. Consequently, when a calculation is made of the percent conversion of SO_2 as a function of contact time, the results are more in keeping with contact times and conversions actually realized in practice.

d. Oxidation of SO_2 on Chromium Oxide Catalyst

Another substance which historically has been known to be effective in catalyzing the oxidation of SO_2 is Cr_2O_3 in conjunction with other metal oxides. Rienacker (Ref.54) noted that, although neither Cr_2O_3 nor SnO_2 alone had any appreciable activity in this regard, their combination was a good contact catalyst for the oxidation of SO_2.

High conversions of sulfur dioxide were reported through the years by several investigators (Ref.55-59) for mixtures of Cr_2O_3 with such metal oxides as SnO_2, TiO_2, and Fe_2O_3. The additons of BaO and Fe_2O_3 with a mixed Cr_2O_3-SnO_2 catalyst were found to increase its efficiency, and the addition of CuO, MgO, SrO, ZnO, Bi_2O_3, MnO_2, CoO and CuO were found to inhibit its activity (Ref.56). NiO and Al_2O_3 seem to vary in their effect on a Cr_2O_3 catalyst, depending on the other metal oxides present (Ref. 55-57).

These catalysts are reported to have typical activation energies of from 19 to 45 kcal/mole between 400-500°C which is comparable to energies of activation obtained with platinum and vanadium catalysts.

Kurin and co-workers (Ref. 60, 61) have studied the kinetics of the oxidation of SO_2 on a Cr_2O_3-SnO_2 catalyst and have fit their results to the following equation:

$$\frac{d\,C_{SO_3}}{dt} = k\,\frac{C_{SO_2} - C^e_{SO_2}}{\sqrt{C_{SO_3}}} \qquad (21)$$

where: C_x is the concentration of component x

C^e_x is the concentration of component x if equilibrium conditions had been obtained

k is the rate constant of the reaction

They measured the rate of reaction at various concentrations of SnO_2 and Cr_2O_3 and also at various temperatures. No support material was used. They found that there were maxima in the catalyst activity which occured at between 2 and 3% SnO_2 and between 30-50% SnO_2. The plotted values of k versus 1/T indicate a break in the curve at about 440°C. These authors attributed this break to a change in mechanism at that temperature. They postulate that the mechanism of the reaction taking place below 440°C is given by reactions a-c and, above this temperature, by reactions d-f, below:

(a) $Cr_2O_3 + SnO_2 \rightleftarrows 2CrO_2 + SnO$

(b) $2CrO_2 + SO_2 \rightleftarrows Cr_2O_3 + SO_3$

(c) $2SnO + O_2 \rightleftarrows 2SnO_2$

(d) $2(Cr_2O_3\ 2SO_3) \rightleftarrows 2Cr_2O_3 \cdot 3SO_3 + SO_3$

(e) $2Cr_2O_3 \cdot 3SO_3 + SnO_2 \rightleftarrows 2(Cr_2O_3 \cdot 2SO_3) + SnO$

(f) $2SnO + O_2 \rightleftarrows 2SnO_2$

There is little in these literature citations that would allow us to decide a priori whether Cr_2O_3 based catalysts could compete with V_2O_5 catalysts for use in flue gas oxidation processes. In a later section, the poison resistance of these catalysts will be discussed showing V_2O_5 and Cr_2O_3 catalysts fairly equivalent in this respect.

e. Oxidation over Iron Oxide Catalysts

A fourth type of catalyst, iron oxide, has, historically, been used almost exclusively by the Soviet Bloc countries for the oxidation of SO_2 (Ref. 62-77).

The reaction can be carried out in two ways to oxidize SO_2. At low temperatures 350°-450°C, (Ref. 73 and 76) sulfur dioxide is oxidized over Fe_2O_3 to form iron sulfate. This latter material is then passed through a furnace where hot gases at 750°-850°C decompose the sulfate and entrain the SO_3. The SO_3 is then absorbed in sulfuric acid.

At higher temperatures 600°-700°C, (Ref.64-66,69) a more truly catalytic process is effected in which SO_2 is converted to SO_3 as it passes through a Fe_2O_3 catalyst bed, sometimes with a CuO promoter. It has been shown, however, that iron sulfate is often an intermediate in this reaction, although it is produced and decomposed in a single process step.

Boreskov (Ref.66) has studied the kinetics of the reaction and found by x-ray examination that above 670°C the catalyst shows only the Fe_2O_3 spacings. Below 670°C, it contains up to 41% of SO_3. The sulfated catalyst is probably a mixture of Fe_2O_3 and $Fe_2(SO_4)_3$. At 680°C, Boreskov found that the rate of reaction was given by:

$$V = k_1 \left(\frac{P_{SO_2}}{P_{SO_3}}\right)^{1.5} P_{O_2} \left(\frac{1}{k_2}\right) \left(\frac{P_{SO_3}}{P_{SO_2}}\right)^{0.5} \qquad (22)$$

Another variation of the catalytic oxidation over iron oxide process is one in which the SO_2 is oxidized in an iron sulfate solution (Ref.68). The reaction consists of two steps. In the first $FeSO_4$ is oxidized to $Fe_2(SO_4)_3$. In the second $Fe_2(SO_4)_3$ is reduced to $FeSO_4$ with the formation of H_2SO_4. During the early stages of the reaction, the optimum temperature is 60°-80°C, and the optimum ratio of SO_2 to O_2 is 1÷5. For the second step, the optimum temperature is 80°-90°C, and the optimum ratio of SO_2 to O_2 is 1:4.

6. Catalyst Poisoning and Effects of Inert Gases

Some discussion of the relative resistance to poisoning of the platinum and vanadium catalysts is found in this report in the section on the comparison of these catalysts. Further review of the effects of inert gases and poisons on the catalyst efficiencies of these systems is provided by Donovan (Ref.78).

The molecular weight of the inert components such as helium, CO_2 and N_2 has a significant effect upon the oxidation rate of sulfur dioxide over vanadium catalyst; the heavier inert gases giving higher rates. This effect has been attributed to the transfer of kinetic energy from inert gas molecules striking the catalyst.

The great number of studies on the effect of water vapor on the activity of vanadium oxide as well as platinum catalysts have produced conflicting results. The only definite conclusion which could be drawn from these studies is that water vapor is certainly not harmful and probably is beneficial to the catalytic oxidation of sulfur dioxide over metal oxide catalysts, at least as long as temperatures are kept high enough to prevent water and sulfuric acid from condensing on the catalyst (Ref. 78 and 79).

The poisoning of catalysts by foreign substances occurs by two widely differing mechanisms. Poisoning occurs most commonly as a result of physical coating or choking of the catalyst and the bed voids by foreign dust. Small amounts of iron sulfate and sulfuric acid in the gas stream tend to aggravate the situation by cementing the catalyst and dust together into an almost impervious mass. This necessitates periodic removal of the layer of catalyst nearest the entrance to the reactor and replacement of it with fresh catalyst.

Another type of poisoning results from chemical reactions between components in the gas stream and the catalyst surfaces. The most effective of these catalyst poisons, as far as the SO_2 oxidation reaction is concerned, is arsenic and its compounds. Susceptibility of platinum catalysts to arsenic poisoning was one of the reasons cited for switching to vanadium catalyst in the contact process. It is reported that 80,000 times more arsenic is needed to deactivate vanadium catalyst, than to deactivate platinum catalyst. Chromium oxide catalysts are reported to have roughly the same resistance to arsenic poisoning as vanadium (Ref.80) and can be regenerated by treatment with carbon monoxide.

The halogens and their compounds are another important class of catalyst poisons. Both chlorine and hydrogen chloride have been found to seriously impair the activity of platinum catalysts. Nearly full activity can be restored by passing heated air over the catalyst, but some platinum is volatilized in the presence of chlorine necessitating periodic addition of fresh catalyst.

The halogens, especially chlorine and fluorine, are felt to be injurious to vanadium catalyst if present in large amounts and for long periods of time. This loss in activity is thought by many to be due to the volatilization of vanadium or V_2O_5 in the presence of halogens.

In contact plants, platinum catalyst masses have lasted as long as 10 years or more before regeneration was required. There have been instances, however, where such a mass only lasted for 2 1/2 years.

Vanadium catalyst, on the other hand, is replaced at the rate of 1/16 of the mass per year, the equivalent of 17 years of catalyst life. Vanadium catalyst is normally not regenerated.

No accurate estimate of the life of a Cr_2O_3 mass can be stated because this type of catalyst is not used in commercial contact acid plants. Little is reported on the stability of Fe_2O_3 to the attack of poisons. However, it is known that the catalyst gradually degenerates because of the formation of iron sulfates (Ref. 81).

7. Oxidation of SO_2 in an Electrical Discharge

Ever since it was shown by Buff and Hoffmann (Ref. 82) and von Wilde (Ref. 83) that sulfur dioxide and oxygen could be passed through an electrical discharge to form sulfur trioxide, this reaction was studied in the hope that it would have some commercial importance. A good review of the work in this area prior to 1939 is that by Glockler and Lind (Ref. 84), and a more up-to-date review is that of Gregory (Ref. 85)

Mahant (Ref. 86) found that SO_2 could be oxidized to SO_3 in the presence of oxygen using an electrodeless discharge. He obtained the maximum conversion (30-40%) with a mixture containing 60% SO_2 and 40% O_2. Mahant reports that no thionates or polythionates were formed by his process. It is clear that it would be impractical for any commercial process to operate with such a high SO_2-to-O_2 ratio and with such low conversion yields.

Poliakoff (Ref. 87) demonstrated that if oxygen alone is subjected to the action of a discharge, it will unite with sulfur dioxide after being removed from the influence of the discharge. Sulfur dioxide was not activated in the same way. This led to the supposition that the reaction proceeded through the attack of ozone molecules, known to form in a discharge, on the SO_2 molecule.

Nechaeva (Ref. 88) observed that the yield of SO_3 formed in a high frequency discharge decreased linearly with an increase of SO_2 content and increase in gas velocity. He found similar results (Ref. 89) for a high voltage arc discharge. However, for practical purposes, he reports that the highest obtainable yield is 66-70% by his method.

In a later paper, Nechaeva (Ref. 90) investigated the effect of the wavelength of the radiation on the oxidation of SO_2 by air in a high frequency discharge. He found that, by changing the wavelength of the radiation, he could change the products of the reaction. At wavelengths of 320 m, O_3 (and then presumably SO_3) were formed primarily, while at a wavelength of 236 m the major products are nitrogen oxides.

All of the above were laboratory scale investigations of the oxidation of SO_2 in an electric discharge. Browne and Stone (Ref. 91) studied this reaction from the point of view of its possible commer-

cial use for removing SO_2 from flue gas. Their conclusion was that 0.09 kw-hr/ft^3 of gas are required to obtain 99% conversion of SO_2 in flue gas. A 75% conversion would require 0.04 kw-hr/ft^3 of flue gas. Based on the 99% conversion figures above, the power consumption and conversion cost per ton of SO_3 produced are 280,000 kw-hr and $1700 per ton, respectively.

These calculations were made using the assumption that the flue gas contains 0.3% SO_2 and that power costs $0.006 per kw-hr. This cost is astronomical compared to the present cost of H_2SO_4($32/ton, 66° Baume; which is approximately equivalent to an SO_3 cost of $40/ton). Browne and Stone's report, that they got appreciable conversion of SO_2 in their test apparatus even with the corona discharge shut off casts some suspicion on their data.

However, even using the more optimistic figures of Gregory (Ref. 85) who reports power expenditures for a variety of materials produced in a corona discharge (not including SO_3) of 8000-25,000 kw-hr/ton, we obtain costs for SO_3 production of $48-$150 per ton.

The conclusion that may be drawn from these studies is that, although it is possible to produce SO_3 from SO_2 and air in an electric discharge, the fact that H_2SO_4 can be produced cheaper by other means makes this method impractical on a commercial scale.

8. Feasibility of Photochemical & Radiation Methods for SO_2 Oxidation

a. Introduction

This section deals with the technical and economic feasibilities of using photochemical and radiation methods to promote or enhance the oxidation of SO_2. A general lack of pertinent data on these methods as applied to SO_2-oxidation makes it difficult to accurately assess technical and economic feasibility. On the basis of some general theoretical and engineering considerations, augmented by the limited experimental data in the literature, some conclusions can be drawn regarding the practicality of these methods. It seems appropriate to list here the various types of applicable radiation and the methods in which they can be used. (See Table 8 below). Practicality or impracticality of each will be shown in the following sections.

b. Direct Irradiation of SO_2-Containing Flue Gases

Untreated or pretreated flue gases can be exposed to radiation such as (a) ultraviolet, (b) particles, (c) particles and electrons, (d) rays, and (e) neutrons.

Table 8

Methods for Radiation Enhancement

Type of Radiation	Direct Irradiation of the SO_2-Containing Gases	Irradiation Pre-Treatment of Catalysts for SO_2-Oxidation	Irradiation of SO_2 Containing Gases in Presence of Catalysts
Ultra Violet	X	-	-
Alpha	X	X	X
Beta	X	X	X
Gamma	X	X	X
Neutrons	X	X	X

One method of evaluating the feasibility of using direct radiation is to estimate the power or activity requirements for this method of SO_2 conversion. For a limiting case, which will yield a low estimate of the power or activity required, the following assumptions can be made:

- all absorbed energy is used uniquely in promoting SO_2 oxidation, i.e., there are no transmission losses, no radiation leaks through the vessel wall, and no radiation energy wasted in producing chemical changes other than the one desired.
- the yield, i.e., the number of chemical changes produced, is proportional to the total radiation dose.
- the yield depends only upon the total dose absorbed rather than the radiation intensity. It will also be assumed that the intensity, i.e., the particle or photon energies, is such that ionization of species does take place.

The proportion of molecules changed can be estimated by:

$$P = 10^{-6} \cdot G \cdot M \cdot R \qquad \text{(Ref. 92)} \qquad (23)$$

where

P = proportion of the molecules changed
G = "G" value, i.e., the number of chemical bonds affected by radiation per 100 electron volt absorbed by the specimen
M = molecular weight of the irradiated species
R = dose rate in megarads

If all of the SO_2 must be converted, i.e., if P = 1, then the dose rate (R) required is:

$$R = \frac{10^6}{G \cdot M} \qquad (24)$$

Excluding irradiation by ultraviolet photons for the time being and limiting the discussion to the other forms of radiation listed above, the needed dose rate can be evaluated if the G value of the SO_2 oxidation reaction is known. No data were found in the literature on G values of this reaction. However, for many chemical reactions in which the total chemical change is proportional to the radiation dose absorbed, a G value in the order of 3 is common. For example, the energy required to produce one ion-pair in air is about 34.5 eV, and the corresponding G value is thus close to 3. It is likely that G will be approximately 3 also for our case since the oxidation of SO_2 proceeds subsequent to the production of oxygen ions. If we take M as 64, then

$$R \cong \frac{10^{-6}}{3 \times 64} \cong 5{,}200 \text{ megarads},$$

a very high dose indeed. The strength of the radiation source necessary can be estimated through the following considerations and assumptions:

- 1 kilowatt hour of energy corresponds to 3.6×10^{13} ergs.
- A radiation dose of 1 Mrad corresponds to an energy absorption of 10^8 ergs per gram of irradiated material.
- Therefore one kilowatt hour fully absorbed can treat 794 pounds per Mrad, or x lbs for 794 lb-Mrad/Kw-hr.
- In general, the following relationship exists

$$x = \frac{794 \cdot W}{R} \qquad (25)$$

where

x = lb of product irradiated per hr with dose of R Mrad
R = dose in Mrad
W = kW output of radiation from the source.

Assuming a power plant emitting 1MMSCFM of flue gas containing 0.5% (volume) of SO_2, the quantity of SO_2 to be oxidized is 106gm moles of SO_2 per second or 54,000 lb of SO_2 per hour. If, in keeping with previous assumptions, it is assumed that only the SO_2 ultimately benefits from all radiation, W, from equation (25), is calculated to be 350,000 kw. A radiation source rated at 350,000 kw output must be provided to handle the oxidation of SO_2 from a power plant which releases 1MMSCFM of flue gas with 0.5% (volume) of SO_2. If the radioisotope source were to be a bremsstrahlung producer such as Sr^{90}, 6.5×10^7 kilocuries of it would be required at an estimated future cost of about $\$13.2 \times 10^9$ (Ref. 93). Also, the quantities required would simply not be available; the projected total productions of Sr^{90} is approximately 300 kw by 1975 (Ref. 93). If the isotope were used as $SrTiO_3$ its weight would be 4.4×10^6 lb.

From these tentative considerations it can be concluded that direct irradiation of flue gases by ionizing radiation is not technically or economically practical. The picture is even less attractive if such factors as radiation losses, shielding and handling problems, depth of radiation-penetration problems, etc. are taken into account.

Literature on photochemical oxidation of SO_2 using ultraviolet (UV) photons is also scant but not nonexistent as was the case for ionizing radiation. In Ref. 94 are examples of such literature. However, measurements of the reaction parameters were typically performed at conditions markedly different from those prevailing in flue gases and the literature data thus may not be pertinent. According to Ref. 94, quantum yields for SO_2-O_2 mixtures varying in ratio of concentration from 1:2 to 2:1 and at UV wavelengths of 1860 Å and 2070 Å, vary from about 0.5 to 3.1. The highest yield occurs at the most energetic wavelength, i.e., at 1860 Å. If such a yield could be achieved in flue gases containing small quantities of SO_2, 2.1×10^{25} ultraviolet photons (λ=1860 Å) per second would be necessary to handle the 0.5 vol % of SO_2 in a 1MMSCFM power plant. This corresponds to an energy of 2.25×10^{14} ergs or 2.25×10^4 kw. It should be stressed, however, that this calculation is based upon data valid for an SO_2-O_2 mixture. It is likely that in flue gases the photons will also interact with the other much more plentiful species and the energy requirement of the ultraviolet source could be very much higher than calculated here. The photochemical approach to SO_2 oxidation does not appear to be attractive. Very large ultraviolet sources would be necessary and their cost would be prohibitive even if the units are available at all. Another problem might be the reliability of the ultraviolet sources at flue gas temperatures.

c. Irradiation Pre-Treatment of Catalysts for SO_2-Oxidation

Reference 95 is an excellent survey of the effects of ionizing radiation on catalysts. Most of the catalyst systems discussed are not pertinent to the problem of SO_2 oxidation. Table 9, extracted from Ref. 95, summarizes research on radiation-treated catalysts for SO_2 oxidation. The platinum catalysts on asbestos substrates show an increase in activity subsequent to exposure to x-ray doses of 1-2 x 10^{18} eV per gram of catalyst. The increase in activity is shown to disappear after a relatively short period of time (12-24 hr). Operation of the catalyst at temperature apparently gradually removes the effects induced by the ionizing radiation. It is evident that the effects of a radiation treatment are of no use in a flue gas reactor, which must operate for extended periods of time. Two examples of radiation-treated V_2O_5 catalysts are listed in Table 9. There appears to be some indication that the activity of V_2O_5 catalysts on a diatomaceous earth substrate is slightly increased if operated at temperatures below 400°C. Whether or not this slight increase in activity exists for extended periods of time could not be ascertained since the literature source cited in Ref. 95 could not be obtained. The nuclear reactor-irradiated V_2O_5 catalyst showed a decrease of activity as compared to the untreated samples. It is perhaps appropriate to stress again the high cost of radiation treatment. Even if the activity of a V_2O_5 catalyst could be improved 10% by a neutron dose rate of 4 x 10^{17} nvt, such improvement would be prohibitively expensive and not practically realizable. For example, neutron fluxes in a thermal reactor irradiation chamber are typically on the order of 10^{14} neutrons/cm -sec. Thus, irradiation periods of 4 x 10^3 seconds would be necessary to achieve an integrated flux of 4 x 10^{17} nvt. For a reference power station it was calculated that 20,000 cu ft of V_2O_5 catalyst would be necessary. If a 10% improvement could be achieved, 18,000 cu ft of radiation-treated catalyst would be required. Total irradiation chamber space, in nuclear reactors in the USA, is usually in the order of a few cu ft or less. Irradiation charges are typically on the order of $7 per cu in. per hr. The cost of the treatment is thus prohibitive, even if the nuclear reactor time could be made available.

From these considerations, it appears that radiation pretreatment of catalysts for SO_2 oxidation is not very promising Many other possible disadvantages of radiation pretreating could be cited. For example, in neutron pretreatment a slight amount of radioactivity can be induced which, in a large quantity of catalyst, could result in major shielding and health problems.

Legend: X: X-Rays
γ: Gamma Rays
n: Neutrons
51/35: Changed from 35 to 51

↑: Increase
↓: Decrease

Tesla Disch: High Voltage Discharge
RT: Room Temperature
α: Day

Table 9

EFFECT OF RADIATION PRE-TREATMENT OF CATALYSTS FOR SO_2 OXIDATION

Catalyst	Reaction	Radiation	Results	Explanation	Remarks
Pt-asbestos	SO_2+O_2, 260°	X18 $2x10^{18}$ ev|gm in moist air	Yield↑,51|35,Return to normal in 24 hr	Radiolysis products of H_2O	No increase in dry air
Pt-asbestos	SO_2+O_2, 300°	X100 $1x10^{18}$ ev|gm in moist air	Yield↑,94|88.Return to normal in∿12 hr	-	No increase in dry air
V_2O_5-K_2O (A) on Diat.earth (B) on SiO_2 gel	SO_2+O_2 400-550°	γ$3x10^{20}$ ev|gm Tesla disch.	(A)Slight↑at 400°, slight↓above 400° (B)∿20%↓at 400°, slight↓above 400°	-	Tesla disch.also effective for (A), not stated for (B)
V_2O_3	H_2+D_2 -78°	γ$4x10^{20}$ ev|gm-78°	↑(5-10)|[1]	-	Stable>1d, RT
V_2O_5-Cr_2O_3 (0-1)	CH_3OH+O_2 →HCHO	nl.$2X10^{20}$nvt thermal	No effect on pure or doped V_2O_5. Doped sample 30-50% more active than pure	Effect below detection if proportional to Cr	0.03%Cr by transmutation
V_2O_5-Ag_2SO_4-SiO_2	SO_2+air 460-520°	n$4X10^{17}$nvt	↓21%,520°;↓33%, 460°	Transmutation* or "polishing by n	*^{110m}Ag

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9. Irradiation of SO_2 Containing Flue Gases in the Presence of Catalysts

A limited amount of literature is available on catalysis in the presence of ionizing radiation. However, no literature was found on catalytic oxidation of SO_2 in the presence of radiation. It would seem that most of the considerations with respect to high cost of large radiation sources and of awkward handling and health hazards discussed above would be equally valid here

10. Liquid Phase Catalysis

The oxides of iron and manganese are both utilized catalytically in aqueous solution to effect the removal of SO_2 from power plant flue gas. However, in each case, the process appears to be unworthy of further development at this time, due to high capital and operating costs. In addition, each represents a high degree of complexity in operation, relative to other proposed processes.

11. Homogeneous Gas Phase Catalysis

Literature reporting the use of gas phase catalytic oxidation of SO_2 was concerned with various applications of the nitrogen oxides. These schemes suffered commonly from high capital and operating costs as presented. Problems include increased residence time (i.e. large gas handling equipment) and loss of catalyst out the stack, which creates additional pollution problems.

C. APPLIED CATALYSIS IN FLUE GAS TREATMENT

1. General

A review of the various processes associated with waste gas cleaning made it necessary to examine any process from which the product was a sulfate. The applications of catalytic oxidation to flue gas treatment, as noted in the literature, fit into three groups on the basis of catalyst type: (1) vanadia, (2) carbon, (3) manganese. These three materials appear to meet the criteria of a catalyst in this application. However, in the case of manganese, only manganous ion is truly a catalyst. Where manganese dioxide is employed in some processes, its action is not truly catalytic because one of the defining criteria for catalysis is that the material remain unchanged chemically at the end of the reaction. It appears more likely that the reaction between sulfur dioxide and dry manganese dioxide proceeds as follows:

$$\overset{4+}{S}O_2 + \overset{4+}{Mn}O_2 \longrightarrow \overset{2+}{Mn}\overset{6+}{S}O_4 \qquad (26)$$

rather than

$$MnO_2 + 1/2\ O_2 + SO_2 \longrightarrow MnO_2 + SO_3 \longrightarrow MnSO_4 + 1/2\ O_2 \qquad (27)$$

Reaction (26) is a straightforward, stoichiometric, redox reaction in which manganese is reduced and sulfur is oxidized.

It became expedient to define catalytic oxidation processes, for the purposes of this review, as those in which sulfur dioxide (or sulfurous acid) is oxidized to sulfur trioxide (or sulfuric acid) in the presence of a material which remains chemically unchanged at the end of the reaction.

All of the processes will be presented with the understanding that only those involving the vanadia, carbon and manganous ion are truly catalytic processes.

A homogeneous catalytic process, a modification of the chamber process is also described although it is not yet in the open literature.

The cost estimates presented for the various processes are our independent estimates based on published information only, standard estimating procedures, and the NAPCA guidelines. We did not use estimates found in the literature for one size plant and scale these estimates up to a 1400 megawatt station.

For some of the processes, there was just not enough information to permit educated guessing on the basis of sound engineering judgment. This is particularly evident in relation to the wet carbon and TVA processes. For one version in each of these categories, there was just enough data to tempt us to "guesstimate" and the cost estimates show it. Consequently, we estimated only one version in each category.

2. Vanadia Based Processes

a. Monsanto-Penelec Process (Ref. 96, 97, 98, 99, 100)

The Monsanto-Penelec process consists of catalytic oxidation of flue-gas sulfur dioxide to sulfur trioxide, which is recovered as sulfuric acid. In 1961, the Pennsylvania Electric Co., Monsanto Company, Air Preheater Co., and Research Cottrell Corp., constructed and operated a small pilot plant at Penelec's generating station at Seward, Pa. Following this, a prototype plant was sponsored by Metropolitan Edison and Monsanto at a generating station in Portland, Pennsylvania. The Monsanto-Penelec process described here, though similar, is not identical with the Monsanto-Metropolitan Edison process, because details of the latter process are proprietary.

The Monsanto-Penelec process is essentially a contact sulfuric acid plant, modified to give high heat economy and low-pressure drop. For high temperature effluent applications (Figure 6) the flue gas is taken from the boiler at 850°-900°F and passed through a high-temperature electrostatic precipitator where virtually all (99.0%) of the fly ash is removed. The gas then flows through a bed of vanadium pentoxide catalyst, with a residence time of 0.3 sec, where the SO_2 is oxidized to SO_3. The gas is then cooled to about 200°F by stepwise passage through an economizer and air preheater. Cooling causes the formation of sulfuric acid mist by reaction of the sulfur trioxide with moisture in the flue gas. Since the condensation begins in the air preheater, both it and the mist eliminator, used to remove the remaining acid, must be made of corrosion-resistant materials.

Sulfuric acid will not condense and cause corrosion if the temperature is above approximately 400°F. It has been recommended that corrosion-resistant materials be used in all areas where the flue gas is below 500°F at design throughputs. The 100°F allowance is provided because the metal will be cooler than the gas being cooled and also the flue gas may be at a lower temperature when operating at conditions other than full load.

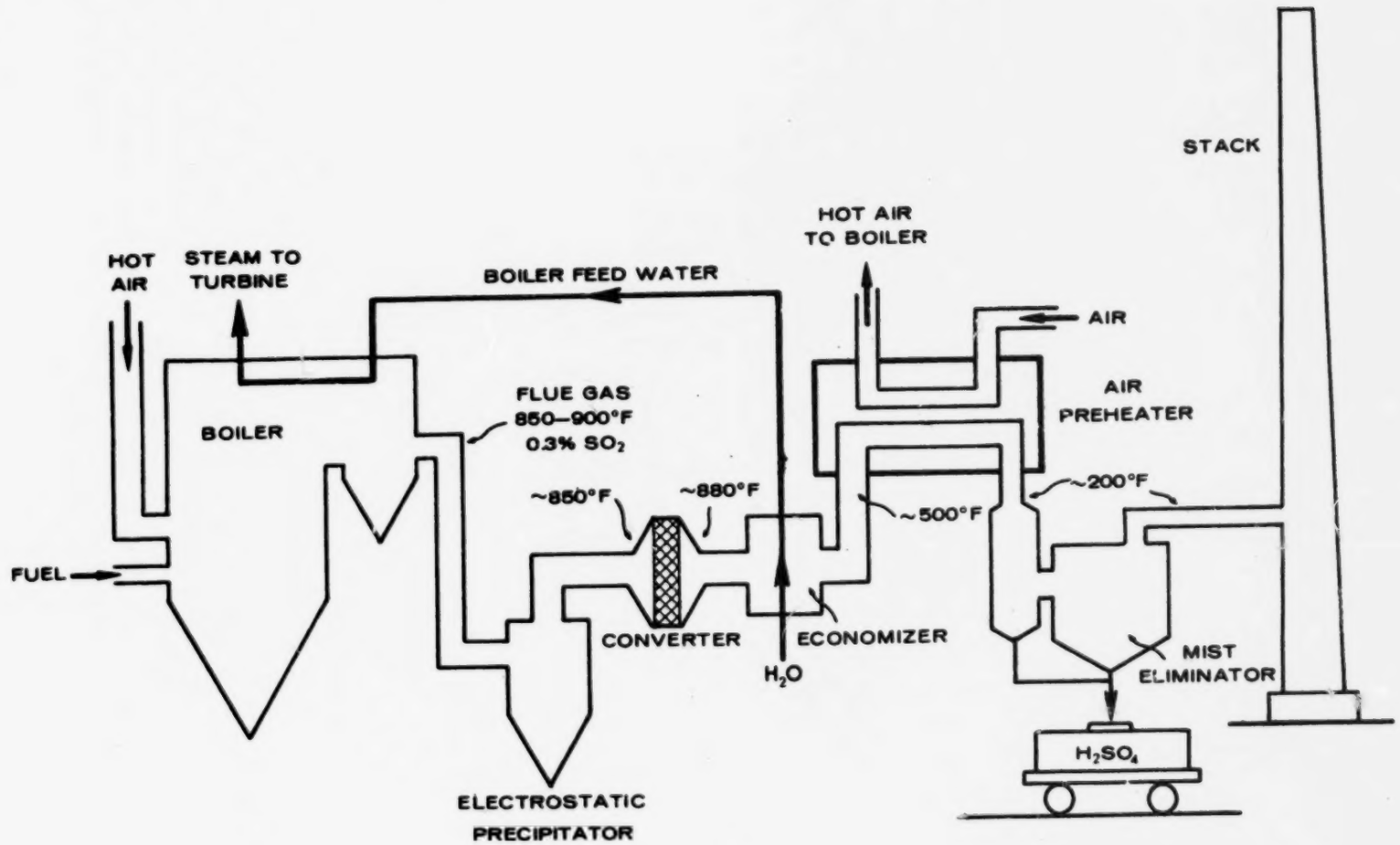
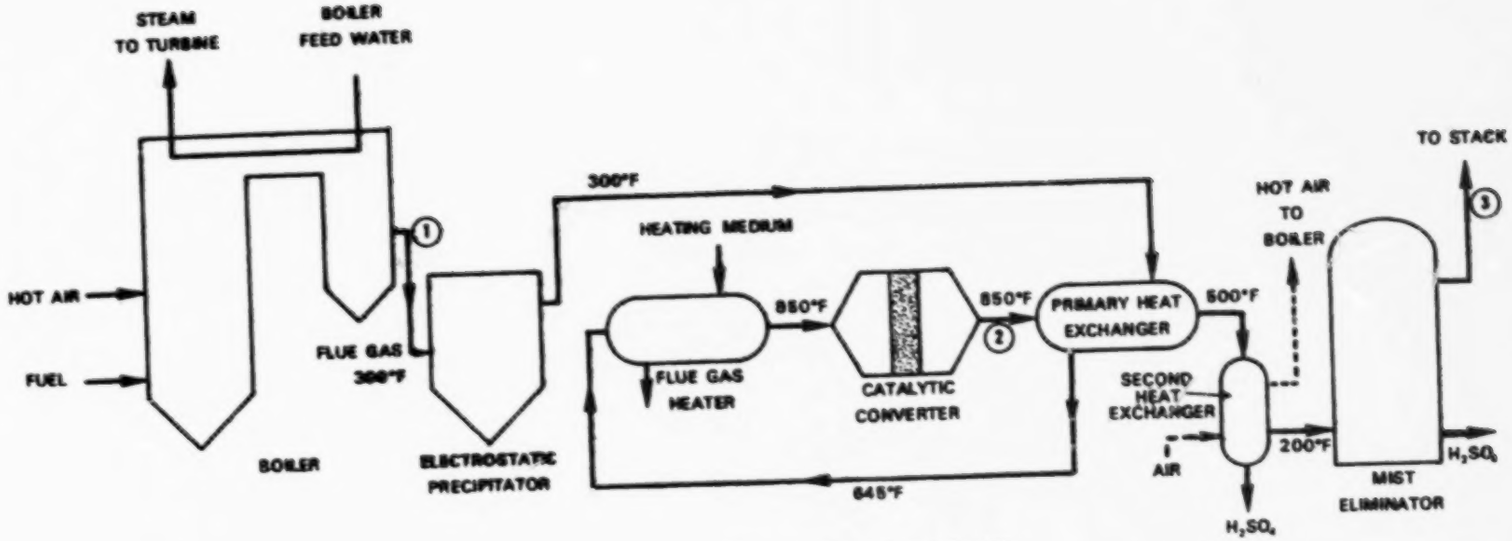


Figure 6. Monsanto-Penelec Process -- New Plant



Flue Gas Rate: 2.5×10^6 SCFM

Stream	Gas flow, vol. % 1	2	3
N_2	74.90	74.95	75.28
CO_2	14.70	14.70	14.83
H_2O	7.25	7.25	6.98
O_2	2.80	2.75	2.86
SO_2	0.30	Trace	Trace
SO_3	-	0.30	Trace
NO_x	0.05	0.05	0.05
Million SCFM	150.0	149.8	148.9

1,715 T/Day 70% H_2SO_4

Figure 7. Monsanto-Penelec Process -- Existing Plant

Figure 7 is a diagram of the Monsanto-Penelec process for an existing power plant as envisioned from various descriptions in the literature. The material balance would be the same for both high and low temperature effluent applications. The obvious point of departure and the major problem in applying the process to existing stations is the requirement of preheating the feed to the converter. We have assumed here that steam will be used as the heating medium. Additional capital would be required for an oil burner to provide hot gas for the heating medium. The possibility of using hot flue gas from the primary boiler for this purpose remains to be explored in detail. The latter would require judicial heat swapping, assuming the appropriate mechanical modifications could be made. In any event, it appears that application of the process to low temperature effluent may be more costly per installed Kw in capital and operating costs than application to high temperature effluent.

The process has several outstanding advantages, i.e., no moving parts are required, problems of recycling an adsorbant are obviated, the final temperature of the flue gas remains essentially unchanged (a problem of considerable magnitude in wet scrubbing processes), and the SO_3 is easily recovered as sulfuric acid.

There are also some disadvantages. The air preheater and mist eliminator must be made of corrosion-resistant material. The saleability of the relatively dilute, 70% to 80% sulfuric acid may present problems, although it may be feasible to concentrate the acid. The electrostatic precipitator for the high temperature effluent from the boiler must be large since it is in the hot zone preceding the converter. Also, the process appears to be more easily applied to construction of new plants than to modification of existing power plants.

b. Kiyoura - T. I. T. Process (Ref. 97, 100, 101, 102)

A process similar to that of Monsanto-Penelec is currently under development by Dr. R. Kiyoura at the Tokyo Institute of Technology (T.I.T.). The process consists of catalytic oxidation of SO_2 by vanadium pentoxide catalyst, but instead of producing sulfuric acid, sulfur trioxide from the converter is reacted with gaseous ammonia to produce solid ammonium sulfate. The Kiyoura - T.I.T. process is presently in the pilot plant stage of development. A large pilot plant, capable of handling 500-1000 cu m/hr of flue gas, was constructed in 1967 and tied into a process steam boiler at the Toyo Koatsu fertilizer plant in Omuta(Kyushu), Japan.

For high temperature effluent applications (Figure 8), flue gas moves from the boiler at about 850°F to a dust collector and then to a catalytic converter where SO_2 is oxidized to SO_3 in a fixed-bed of vanadium pentoxide catalyst. After cooling to about 500°F, the gas stream receives ammonia which prevents condensation of sulfuric acid, since it reacts to form ammonium sulfate.

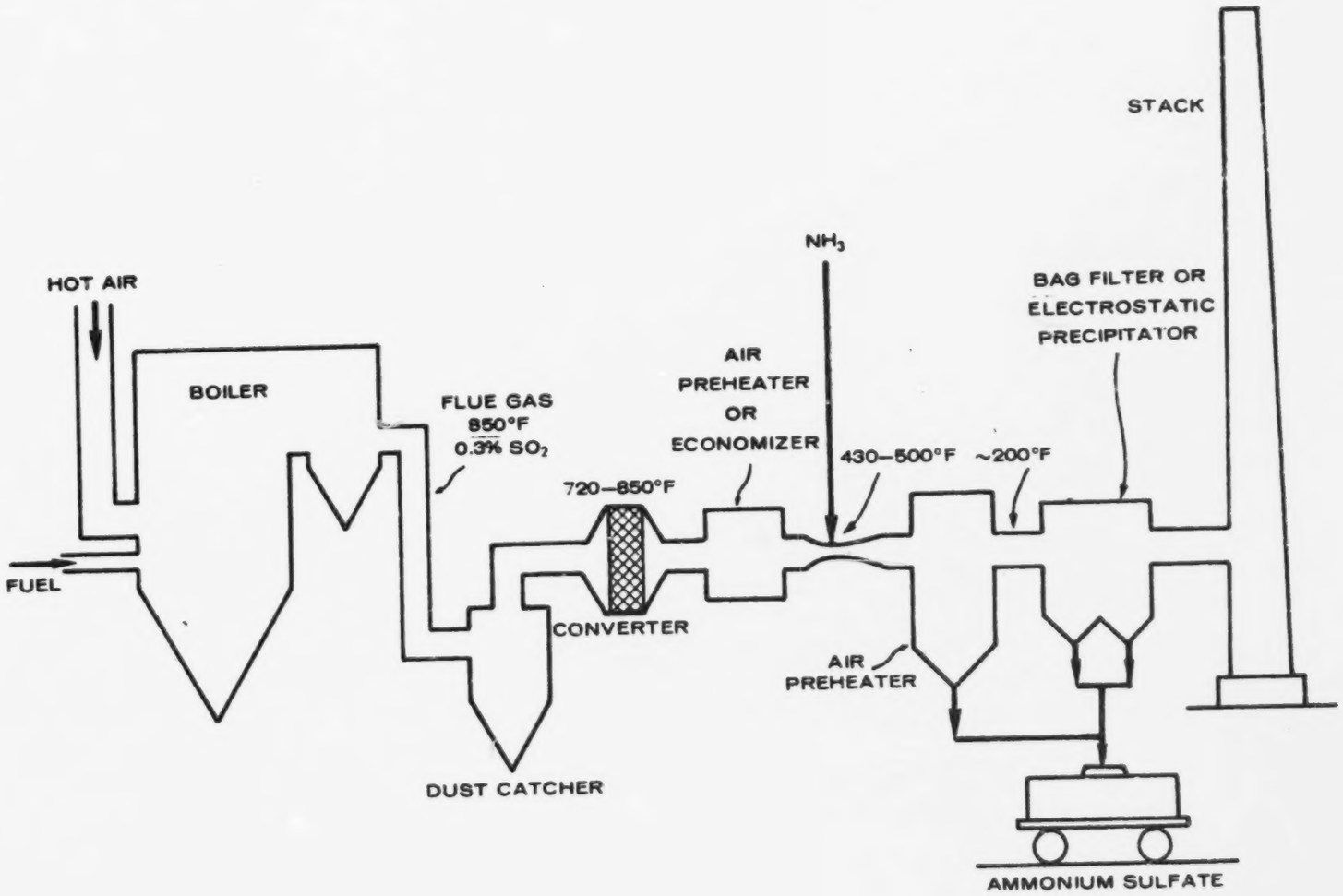
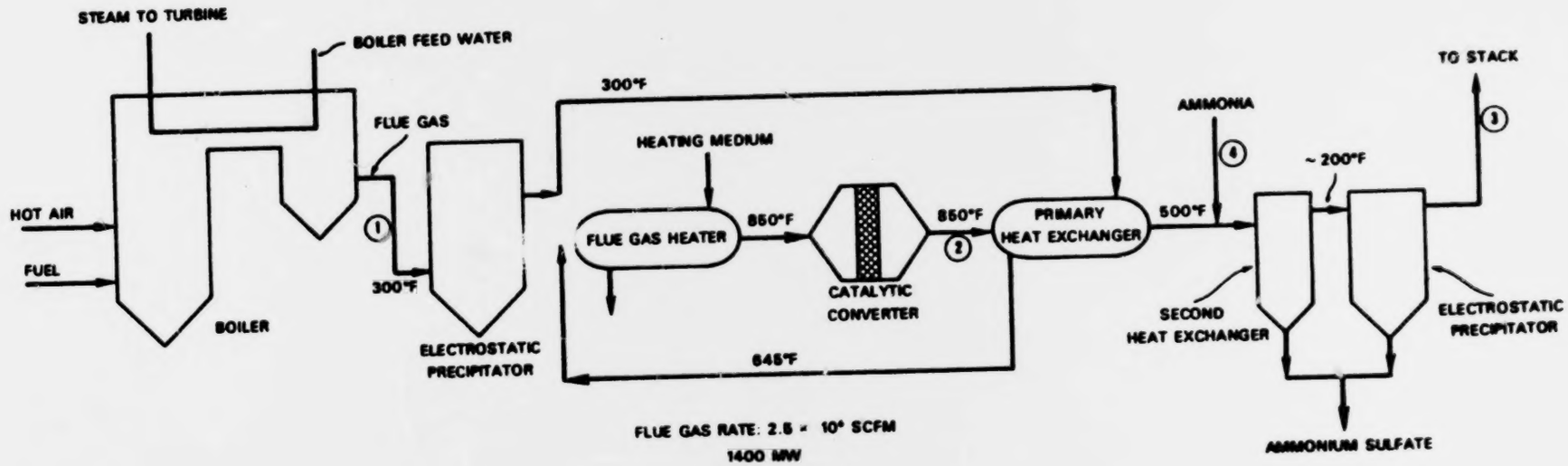


Figure 8. Kiyoura-T.I.T. Process -- New Plant



FLUE GAS RATE: 2.5 × 10⁶ SCFM

1400 MW

GAS FLOW, Vol. %

Stream	1	2	3	4
N_2	74.90	74.95	75.28	-
CO_2	14.70	14.70	14.83	-
H_2O	7.25	7.25	6.98	-
O_2	2.80	2.75	2.86	-
SO_2	0.30	Trace	Trace	-
SO_3	-	0.30	Trace	-
NOx	0.05	0.05	0.05	-
NH_3	-	-	-	100
Million scfh	150.0	149.8	148.9	0.774

1,620 T/Day $(NH_4)_2SO_4$

Figure 9. Kiyoura-T.I.T. Process -- Existing Plant

The temperature at which ammonia is reacted with the flue gas (420°-500°F) is apparently very important. In this temperature range, crystals of 1-3μ and aggregates of >100μ of pure ammonium sulfate, suitable for bagging and shipping, are produced.

Figure 9 shows a flow diagram of a low temperature effluent version of the Kiyoura process. The material balances for both high and low temperature effluent applications are the same. The major difference in cost for these versions was due to the requirement for a flue gas heater for the low temperature application.

The process has essentially the same advantages as the Monsanto-Penelec process, in that no moving parts are required, the temperature of the flue gas remains essentially unchanged, there is no problem of recycling an adsorbent and the sulfur trioxide is easily recovered as $(NH_4)_2SO_4$.

In addition to these advantages the method avoids the expense of a corrosion problem associated with acid condensation and allows shipment of a dry product rather than a liquid one.

Among the disadvantages of the process are: (1) the requirement for an additional precipitator (or a bag house), (2) either discharging the flue gas at (or about) 400°F or adding another heat exchanger, and (3) the cost of ammonia and its system. Although it is not mentioned, it appears that very precise control of the ammonia/sulfur dioxide reaction is necessary to prevent, or minimize, escape of either reactant. The process also creates the problem of product marketability in the U. S. where ammonium sulfate has a low market value and demand.

c. Bayer Double Contact Process (Ref. 103, 104, 105)

The Bayer double contact process is primarily a means of increasing the overall conversion in a commercial, contact sulfuric acid plant. Normally, in a contact sulfuric acid plant, conversion is 97-98%, with the residual 2-3% unconverted SO_2 exhausted to the atmosphere. In the double contact process, conversion is carried to about 90% at at which point the product SO_3 is absorbed from the gas mixture. This effects a shift in the mixed gas composition away from the near-equilibrium condition, and consequently enhances the conversion rate in a final contact pass. The process not only achieves overall conversion of 99.5% but, in so doing, virtually eliminates SO_2 emission from this source. The achievement is costly, however, because of an additional absorption step and the requirement to reheat the gas stream for the second contact pass. It is noted that the economics are favorable only where the price of sulfuric acid justifies the added cost and that even in such circumstances the economics become marginal when SO_2 concentration in the feed stream drops to about 9%.

It appears that the double contact process would not be applicable to removal of SO_2 from flue gas and would be of no benefit even in the case of a 5% SO_2 smelter gas. The "breakeven" concentration of SO_2 for double contact operation is 6%.

3. Carbon Based Processes

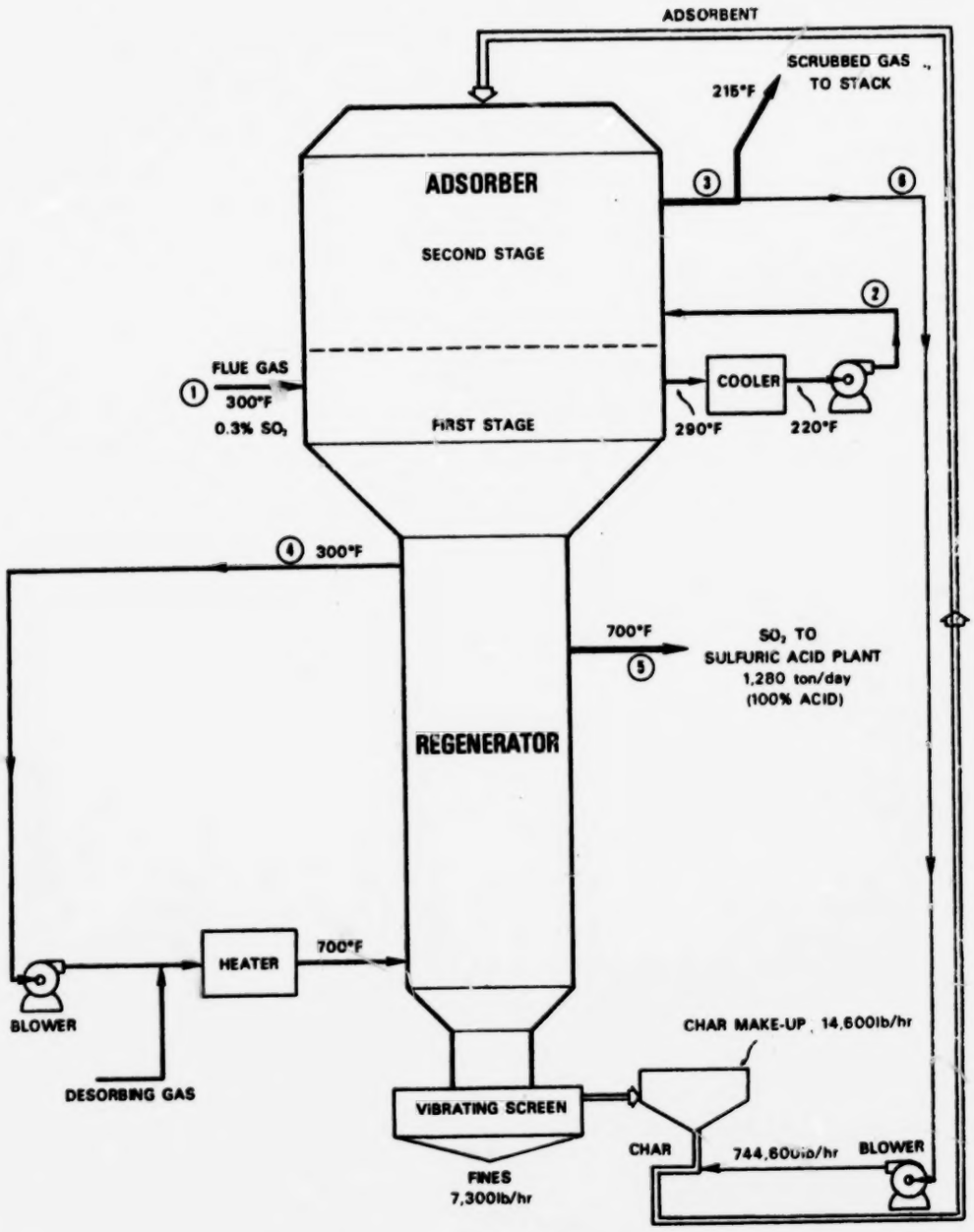
a. Reinluft Process (Ref. 96, 97, 98, 99, 117, 120, 123)

The Reinluft process for removal of sulfur oxides from power plant stack gases was invented several years ago at Reinluft Gmbh, Essen, Germany, by Dr. F. Johswich. The dry process utilizes activated char to catalyze the oxidation of sulfur dioxide to sulfur trioxide at a relatively low temperature. The char acts as an adsorbent for the sulfuric acid that forms from the reaction of the trioxide with moisture in the gas stream. At high temperature, the sulfuric acid dissociates into water and sulfur trioxide. The sulfur trioxide is reduced to the dioxide by reaction with the carbon, thus reactivating the adsorbent. The desorbed sulfur dioxide may be converted into elemental sulfur or sulfuric acid.

The Reinluft process has been at a more advanced stage of development than any other known dry process. The Volkswagen works at Wolfsburg operated a small plant for several years and were the first to acquire one of the three prototype units. A second plant was built at the Carbosulf Company at Cologne. The 1.9 million cu ft per hr plant was designed to run on a mixture of sulfuric-acid-plant tail gas and waste gas from a Claus-process kiln. The third unit is the Luenen installation in November 1966 alongside an experimental power station operated by Steinkohlen Electricitat AG. It is designed to treat about 1.15 million cu ft per hr of flue gas containing up to about 0.9 grain/cu ft of coal dust. The operating level of the Luenen unit corresponds to that of a power station of about 11-Mw output, which is about the level of the unit at Cologne also.

In England, active interest has been shown in the process. The Department of Scientific and Industrial Research has purchased a pilot-sized plant of the Reinluft design to treat 16,000 cu ft/hr of flue gas from an oil-fired furnace at their Warm Spring laboratory.

The system consists of a two-stage adsorber section located over a desorber section, as shown by the flowsheet in Figure 10. The adsorbent enters at the top of the second stage and moves downward against the gas stream at a rate of 1 to 2 mm/min. The temperature in this larger stage of the adsorber is about 220°F. Flue gas, at 250° to 320°F, enters the unit via the first (lower) stage which acts as a primary high-temperature stripper to remove all sulfur trioxide and sulfuric acid initially present in the gas. Since the oxidation of sulfur dioxide is accomplished at a relatively low temperature, the gases are drawn off, cooled to 220°F and returned to the adsorber, entering at the second stage. The clean gas then emerges at the top of the unit, having lost up to 99.9% of its original sulfur dioxide content. Meanwhile, the 10



	Gas Flow, Volume %					
Stream	1	2	3	4	5	6
N_2	74.9	74.9	75.02	28.05	28.05	75.02
CO_2	14.7	14.7	14.73	18.10	18.10	14.73
H_2O	7.25	7.25	7.33	27.80	27.80	7.33
O_2	2.8	2.8	2.87	1.05	1.05	2.87
SO_2	0.3	0.3	Trace	25.00	25.00	Trace
NO_x	0.05	0.05	0.05	-----	-----	0.05
SO_3	----	-----	-----	-----	-----	-----
Million SCFH	150.00	150.00	149.57	13.20	1.72	2.6

Figure 10. Reinluft Process for SO_2 Removal

to 12 mm lumps of adsorbant, loaded with sulfuric acid, move down through the adsorber into the desorption section. Here the temperature is raised to 700° to 750°F. Heat is supplied by product gas circulating at 300°F from near the top of the regenerator, through a heater, and into the bottom of the desorber (regenerator). In this section, the sulfuric acid dissociates into SO_3 and water, and the SO_3 reacts with the carbon to form the product gas, CO_2 and SO_2. A side stream of the product gas containing approximately 25% SO_2 is withdrawn for subsequent processing. It is not necessary to place the regenerator under the adsorber. In another arrangement, the regenerator could be alongside.

In the regeneration, other sulfur-bearing material likewise reacts to form sulfur dioxide. At this temperature level (700° to 750°F), side reactions forming carbon monoxide or undesirable sulfur compounds do not occur and the bond between the activated carbon and sulfur dioxide is so weak that a comparativley small stream of scavenging gas (CO_2 or N_2) is sufficient to flush away the dioxide.

Reduction of the SO_3 to SO_2 during desorption acts to regenerate the slowly moving charcoal bed. Char is added to the adsorbant leaving the desorber to make up for losses by reaction with SO_3 and production of fines. Before recycle, the adsorbant is screened to remove the fines.

The process uses low-temperature coke as the adsorbant instead of activated carbon. The coke is formed by vacuum-carbonizing of coal, lignite, peat, wood, or tarry material at about 1100°F. Although the raw coke is not "activated," single or repeated impregnation with sulfuric acid and subsequent evaporation at the high temperature turns it into an effective adsorbant material. At the treatment plant, the low activity fresh coke is used as the make-up. After three to ten cycles, the activity of the adsorbant reaches a maximum corresponding to that of the best gas-adsorption charcoal.

The process has several advantages. Gas cooling is not excessive, corrosion-resistant equipment is not required, and the by-product, SO_2, may be used either to produce sulfuric acid or elemental sulfur. Reduction of the trioxide consumes part of the carbon and renders the granules porous. This is equivalent to activation in place so it mitigates the relatively high cost (cost of low-temperature coke in Germany is $25 to $90 per ton; activated carbon is $750 to $1250 per ton) of activation beforehand. However, because part of the carbon is consumed, it must be replaced. Make-up requires about 0.2 lb of adsorbant per lb of sulfur adsorbed.

Among the disadvantages of this process is the cost of recirculating the very large amount of carbon required, as well as, the cost of heat and reducing agent. A very prominent disadvantage is the instability of low-temperature coke in the presence of flue gas oxygen. Startups were frequently beset by uncontrollable oxidations and the development of hot spots. This was particularly noted in a large-scale plant at Cologne which resulted in the redesign of adsorber internals for a unit at Luenen (near Dortmund) to prevent

heat accumulation. As an additional safety measure, the Luenen plant also had a large vessel installed into which all the activated coke can be dumped if there is a tendency to overheat. At first, it appeared that the problem might be overcome, but according to our latest information the process has been abandoned both in England and Germany.

b. Sulfacid Process (Ref. 97, 124, 125)

The Sulfacid process was developed by Lurgi (Lurgi Gesellschaft fur Chemie und Huttenwesen mbH, Frankfurt) in Germany for removal of sulfur dioxide mainly from flue gases other than power station gases. The principal difference between this and the Reinluft process is the method of regenerating the carbon catalyst. The Sulfacid process washes the catalyst to remove the by-product sufuric acid.

The process has been tested in two plants, operating downstream of oil-fired boilers with flue gas rates of 35,000-53,000 cu ft/hr, respectively. Two commercial plants are in operation which remove more than 90% of the SO_2 from detergent sulfonation waste gases at flow rates of 35,000 and 88,000 cu ft/hr, respectively. Also operational are two plants utilizing flue gases containing 4 g SO_2/cu ft from oil-fired equipment with capacities of 53,000 to 105,000 cu ft/hr. The process is scheduled for treating the waste gas from a 300-ton/day sulfuric acid plant, and plans are underway for testing the process in a coal-burning power plant as well.

The conversion of sulfur dioxide to sulfur trioxide and sulfuric acid takes place in a fixed, carbon-containing catalyst bed below 220°F when cooled flue gas is passed through (Figure 11). Sulfur dioxide is adsorbed on the catalyst where it reacts with oxygen adsorbed from the gas stream and then moisture to form sulfuric acid. The acid formed in the catalyst pores is continuously rinsed out by a water spray. The clean, cooled flue gas is exhausted to the atmosphere.

Acid obtained from washing the catalyst bed is about 10-15% H_2SO_4. It is concentrated during the cooling of the entering flue gas from about 300°F to the reactor temperature (140°-160°F). In a packed-tower with countercurrent scrubbing, the acid concentration can be increased to 60-70%, depending on the flue gas temperature. However, when a large volume of gas is to be processed, as from a power plant (or when the gas is rich in fly ash), a Venturi scrubber is required for cooling. In this case, the maximum attainable acid concentration is only 25-30% due to the co-current operation of the scrubber.

The catalyst mass is essentially activated carbon, although special additives have been used to accelerate oxidation of the sulfur dioxide. Formation of sulfuric acid in the catalyst apparently acts to clean the bed, as no loss in activity of one bed was noted after three years of treating the stack gas of a sulfuric acid plant.

The Sulfacid process is simple and avoids the fire-hazard disadvantage of the Reinluft process. However, there is considerable cool-

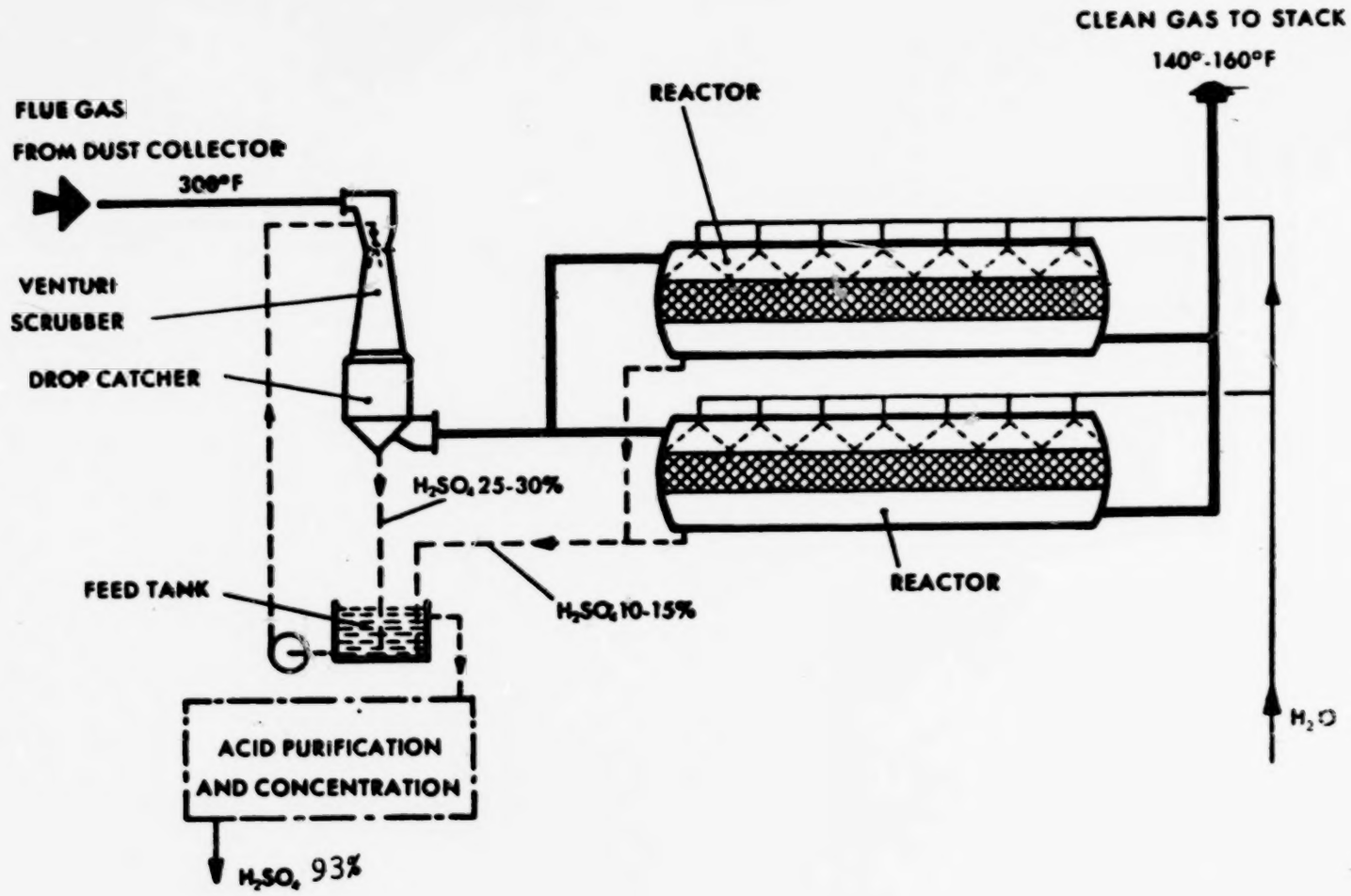


Figure 11. Lurgi Sulfacid Process for SO_2 Removal

ing of the exhaust gas (to 140°-160°F), and the wet, fixed catalyst beds create a considerable pressure drop in the gas stream. The sulfuric acid product requires corrosion-resistant construction materials. Scrubbers and packed towers for cooling and concentrating, and the converter, are reportedly of mild steel with lead or rubber lining.

c. Hitachi Process (Ref. 97, 126)

A process similar to the Sulfacid process is under development by Hitachi Ltd. at the Goi plant of Tokyo Electric Power Company where a 2 Mw test unit is in operation.

The system (Figure 12) consists of six towers charged with activated carbon catalyst. The towers operate in a cyclic manner: a single tower goes through a cycle of 30 hrs of adsorption of SO_2 from uncooled (300°F) flue gas from the dust collector, 10 hrs of washing (during which, no gas passes through the tower), and 20 hrs of drying. At one time, three towers are adsorbing SO_2, two towers are drying and one tower is being washed. Therefore, the gas flow in the system is changed every ten hours, and the total time of one cycle becomes 60 hrs.

After 30 hrs of dry adsorption, the gas flow through a tower is stopped and water enters the top of the tower to wash the sulfuric acid from the carbon. The acid, formed directly on the carbon during the adsorption period is about 70% H_2SO_4. Acid concentration in the wash, however, is only 10-20% H_2SO_4, and even this level is attained only through a type of staged, counter-current washing operation.

Wet carbon, previously washed to remove sulfuric acid, contains 20-50 wt % water and is dried by hot flue gas. The temperature of the gas in the drying section drops to 120°-160°F until the carbon is dry, at which time the gas temperature rises to that of the entering flue gas, ca 300°F. There is some adsorption of SO_2 during drying so that the net total adsorption time in a 60-hour cycle is 50 hours.

Gas from the drying section is mixed with flue gas from the feed blower and enters a dry adsorption tower where SO_2 and moisture from the drying section are removed. The humidity of the gas stream to the atmosphere is thus very near that of the flue gas from the boiler. Heat of adsorption and reaction result in a temperature rise of 10°-30°F during adsorption to give a net temperature drop in stack gas temperature of only about 55°F.

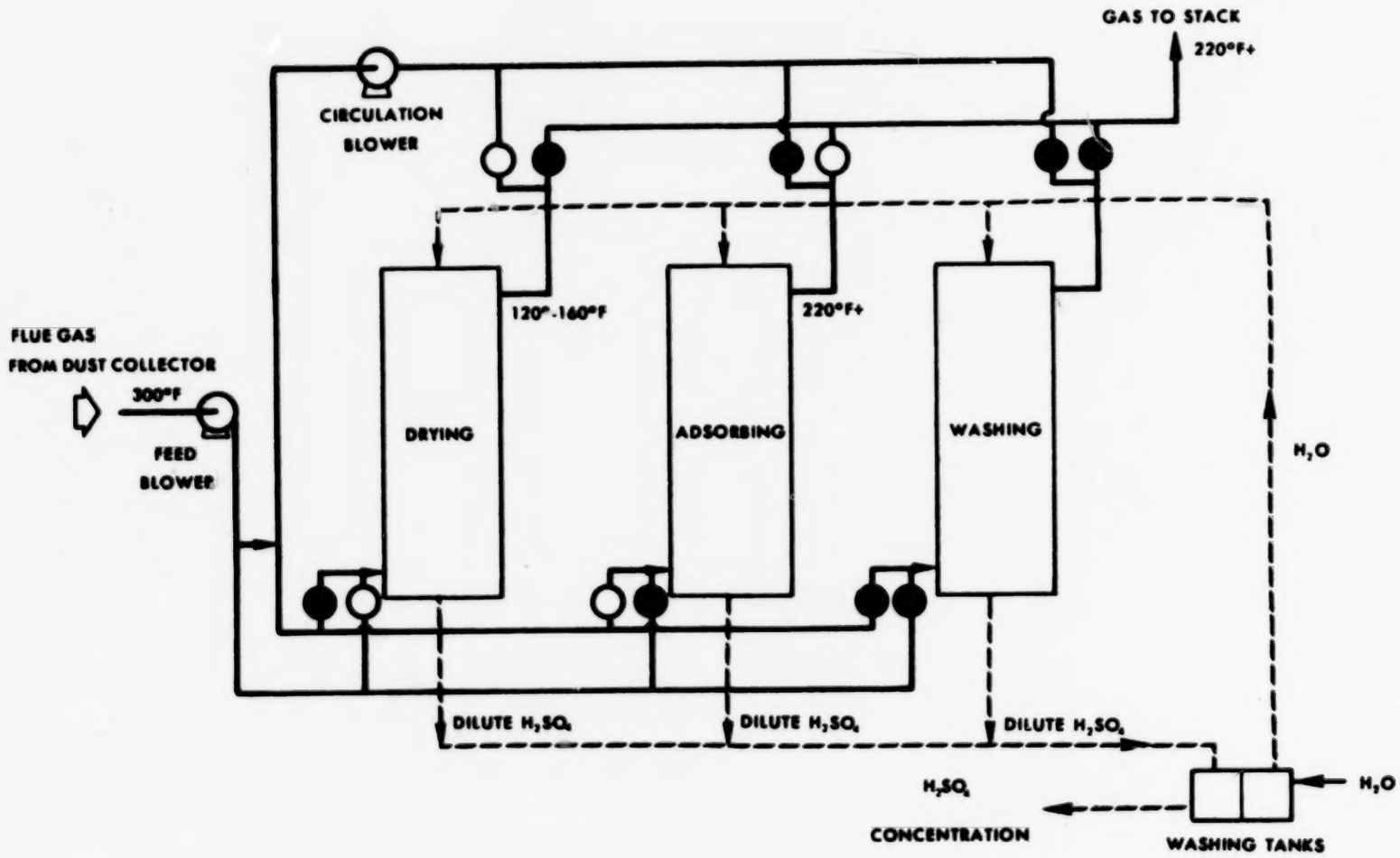


Figure 12. Hitachi Process for SO_2 Removal

The equipment for a process plant would include the following:

- Six towers containing activated carbon.
- Feed blower.
- Circulation blower.
- Pump for wash water.
- Purge pump.
- Tanks for storing washings.
- Acid concentration equipment.
- Dampers for changing gas flow from tower to tower.

The process has the advantages and disadvantages of the Sulfacid process. Investment costs in corrosion-resistant materials and dampers would be high; the acid concentration is low and would involve increased cost for processing. Some pressure drop in the fixed bed would occur; however, compared with Reinluft, the process is safe, and the effect of the process on stack gas temperature is small; the exhaust temperature of the gas is over 220°F. The process is simple in principle, removal of the H_2SO_4 is easy, and there appear to be no drying problems. Furthermore, the process removes more than 90% of the SO_2 from power plant stack gas.

4. Manganese Based Processes

a. Mitsubishi Process (Ref. 97, 110, 114)

Mitsubishi Heavy Industries Ltd., Tokyo, has a process for removal of sulfur dioxide from flue gases that relies on the reaction of sulfur dioxide with manganese dioxide to form manganese sulfate. Regeneration of the manganese dioxide is accomplished by reaction of the sulfate with ammonia. Ammonium sulfate is produced as a by-product.

Mitsubishi originally tested the process at the Yokkaichi oil-burning power station of Chubu Electric Power Company. The small test unit treated gas equivalent to about 1 Mw. Following the success of the pilot plant study, a large desulfurization unit was built at the same location to process 25% of the flue gas output of the 220 Mw oil-burning power plant.

The Mitsubishi process (Figure 13) is composed of the following three major units:

A. Gas adsorption units consisting of adsorption tower, multiclone, electrostatic precipitator, blower and absorbent feeder.

B. Regeneration units consisting of oxidizing tower, ammonia scrubber, air compressor and filter.

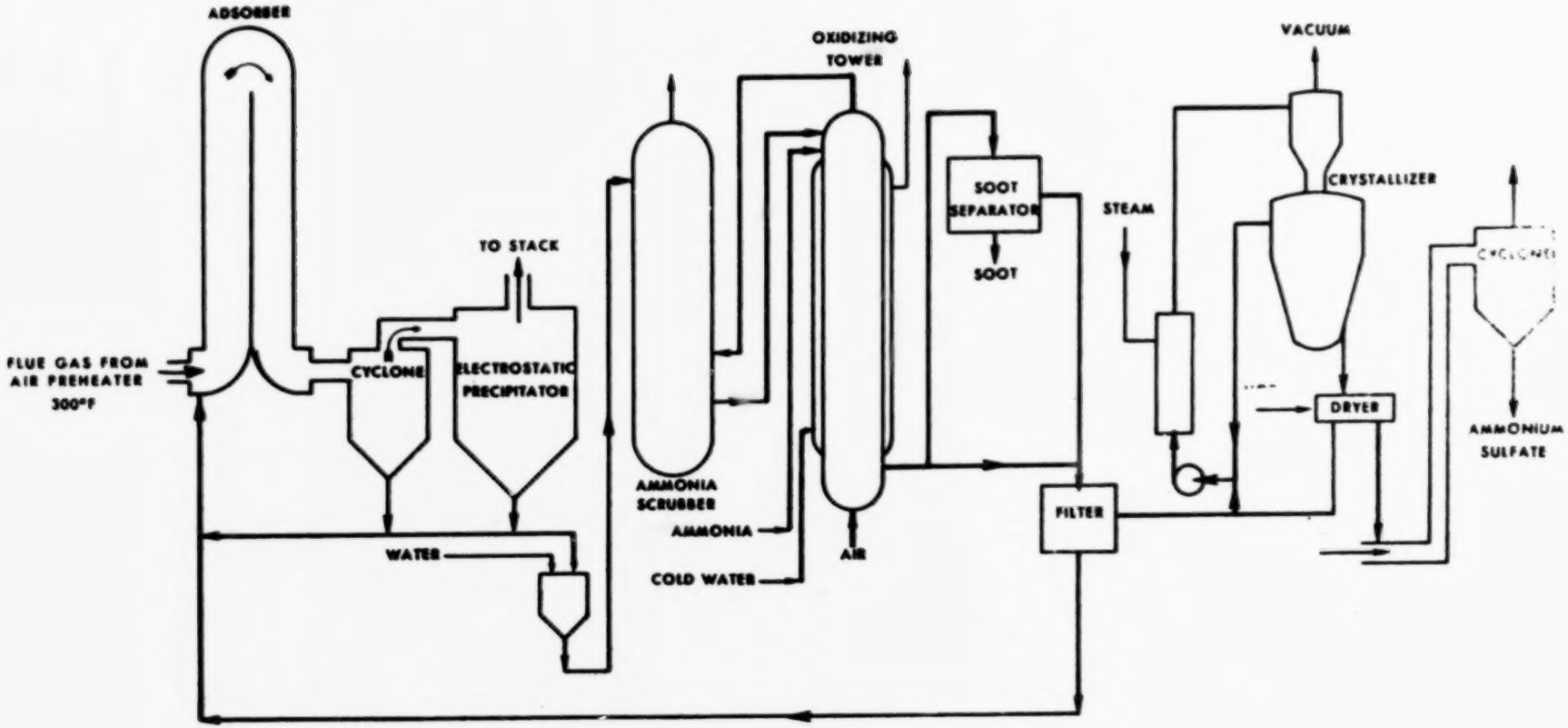


Figure 13. Flow Diagram of Mitsubishi Manganese Dioxide Process

C. Crystallizing units consisting of reactor, crystallizer and dryer.

Flue gas from the air preheater enters an adsorption tower into which active powdered manganese dioxide is uniformly dispersed. The moving bed adsorber is said to be suitable for large volumes of flue gas containing low amounts of sulfur dioxide. The linear velocity of the gas is increased by about 50% in the adsorber. The temperature of the gas remains between 212° and 356°F. The amount of adsorbent used in the unit is 150 to 250 g/cu m. flue gas.

In the adsorber, sulfur dioxide reacts with manganese dioxide to form manganous sulfate. The exit gas enters a cyclone, where about 90% of the unreacted manganese dioxide, and the manganese sulfate, are collected and returned to the gas stream entering the adsorption tower. The residual 10% of the solids mixture is collected in an electrostatic precipitator. The adsorbent exists as relatively large 40μ high density particles. From 203° to 257°F the resistivity of the adsorbent is between 3×10^{-7} and 8×10^{-7} ohm-cm. This and the size allow trouble-free collection in the electrostatic precipitator.

From the precipitator, solids are sent to a tank and slurried with about 70% water. The slurry is passed through an ammonia recovery tower and into the regenerator (oxidizing tower). Air and ammonia are injected into the regenerator where hydrated manganese oxides and ammonium sulfate are produced. The solid oxides are separated from the ammonium sulfate solution by filtration and returned to the flue-gas inlet. The ammonium sulfate solution goes to a crystallizer for recovery of the solid product.

For an oil-burning power plant, flotation with kerosene was used to remove soot or ash from the slurry at the soot separator. This was found to lengthen the useful life of the adsorbent and improve the purity of the ammonium sulfate.

There are several advantages to the Mitsubishi process. Because it operates at stack gas temperature, it is easily adapted to existing power plants. The exhaust gas is still dry and warm after treatment providing favorable plume characteristics. Mild steel fabrication is indicated throughout, except in slurry treating units. Low pressure drop in the adsorber suggests economical movement of gas through the treatment unit.

Among the disadvantages of the process is the fact that the by-product, ammonium sulfate, has essentially no market potential in this country. In Japan, or other parts of Asia, the product market potential may be brighter. Though simpler than most systems for this type of process, the manganese dioxide regeneration is still

complex. As the station size increases, the materials handling problem associated with the adsorbent also increases until, at the 1400 Mw level this amounts to moving 16 tons/min of adsorbant.

b. TVA Ozone-Manganese Processes (Ref. 106, 107, 109, 112)

In the process variations of direct acid process and direct ammonium sulfate process, manganous ion appears to be acting as a true catalyst. However, unless ozone acts as a separate catalyst, its obscure role in conjunction with manganous ion might be considered unnecessary.

In the direct acid process, (Figure 14), ozone, at concentrations up to 240 ppm, is injected into the flue gas stream. The gas is then cooled to 130°-170°F and scrubbed in a packed tower with a liquor consisting of sulfuric acid and manganous ion, the latter in concentration from 0.02% to 0.2%. In the scrubbing tower, sulfuric acid is produced at a maximum concentration of 40%. The weak acid can be concentrated in cooling the entering flue gas to scrubbing temperature. No provision is described for removing manganous ion from product acid. Conceivably, this may not be important to product use, but it represents considerable loss of manganese.

In the direct ammonium sulfate process, Figure 15, the scrubbing liquor consists of ammonium sulfate solution and manganous ion in the same concentration as above. Operation is essentially the same, except that the sulfuric acid formed is continuously neutralized with ammonia. The ammonium sulfate solution can be concentrated, to some extent, in cooling the entering flue gas; but, to produce a dry product, considerable additional equipment would be required. Again, there is no description of manganous ion removal from the product.

In both processes, retention times in the scrubbers ranged from 18 to 36 seconds, with better performance at higher retention time. The major part of TVA's study was done with simulated flue gas consisting of 0.35% SO_2, 3.5% O_2, 16% CO_2 and 80% N_2. The composition corresponded approximately to gas produced by burning coal containing 3.5% sulfur with 10% excess air. In tests with flue gases from a power-plant and a pilot plant coal burner, the process was far less efficient; recovery of a high percentage of SO_2 required a retention time on the order of 90 sec. The efficiency of ozone utilization, even with a retention time of 90 sec, was very low.

Apparently, some component in the combustion gas poisons the catalysis. Thorough removal of particulate matter did not improve per-

formance indicating the poison(s) to be gaseous. The identity of the poison(s) was not determined; however, phenol, sometimes found in coal combustion gases, is known to poison manganese catalyst.

These processes are saddled with far more disadvantages than advantages, perhaps the greatest disadvantage in relation to large power stations, is the long residence time of the gas in the scrubber.

5. Selenium-Based Processes

Recently, two processes have been described for removal of SO_2 from flue gas based on the stoichiometric reaction

$$2SO_2 + SeO_2 + 2H_2O \longrightarrow Se + 2H_2SO_4 \qquad (28)$$

This wet-process reaction proceeds at a rate roughly 10 times the rates obtained with wet reactions employing elemental oxygen catalyzed by ozone, manganese ion, or carbon. The possibility of completely and economically removing SO_2 derives from the fact that the selenium is precipitated in solid form and is insoluble in the product acid. The reaction is therefore irreversible and proceeds to completion. Elemental selenium is readily filtered out permitting recovery of a "clean" product acid, a distinct advantage over the manganese wet processes. Selenium is converted back to the dioxide by "burning" it in air. Since the dioxide sublimes at about 350°C, a means is thus afforded of separating the material from residual fly ash contamination.

a. Nor Deutsche Affinerie Process (Ref. 127)

In the Nor Deutsche process, Figure 16, flue gas passes through two scrubbing towers sequentially. In the second tower, the gas is scrubbed with a solution of selenous and sulfuric acids in which the concentration of selenium dioxide is maintained constant and in excess of that required to oxidize the SO_2, some of which was removed in the first tower. The exhaust gas from the second tower is essentially free of SO_2 and vents to the stack. Selenium is continuously filtered out of the recycle scrubbing acid, oxidized, and redissolved in the scrubbing acid. Aliquots of the scrubbing solution are withdrawn at intervals from the second tower and sent to the first tower where recycle continues until all of the selenium dioxide is reduced by incoming flue gas to selenium-free product. Product acid leaves the system through a concentrator heated by incoming flue gas. It is claimed that 60° Be sulfuric acid is attainable in this manner.

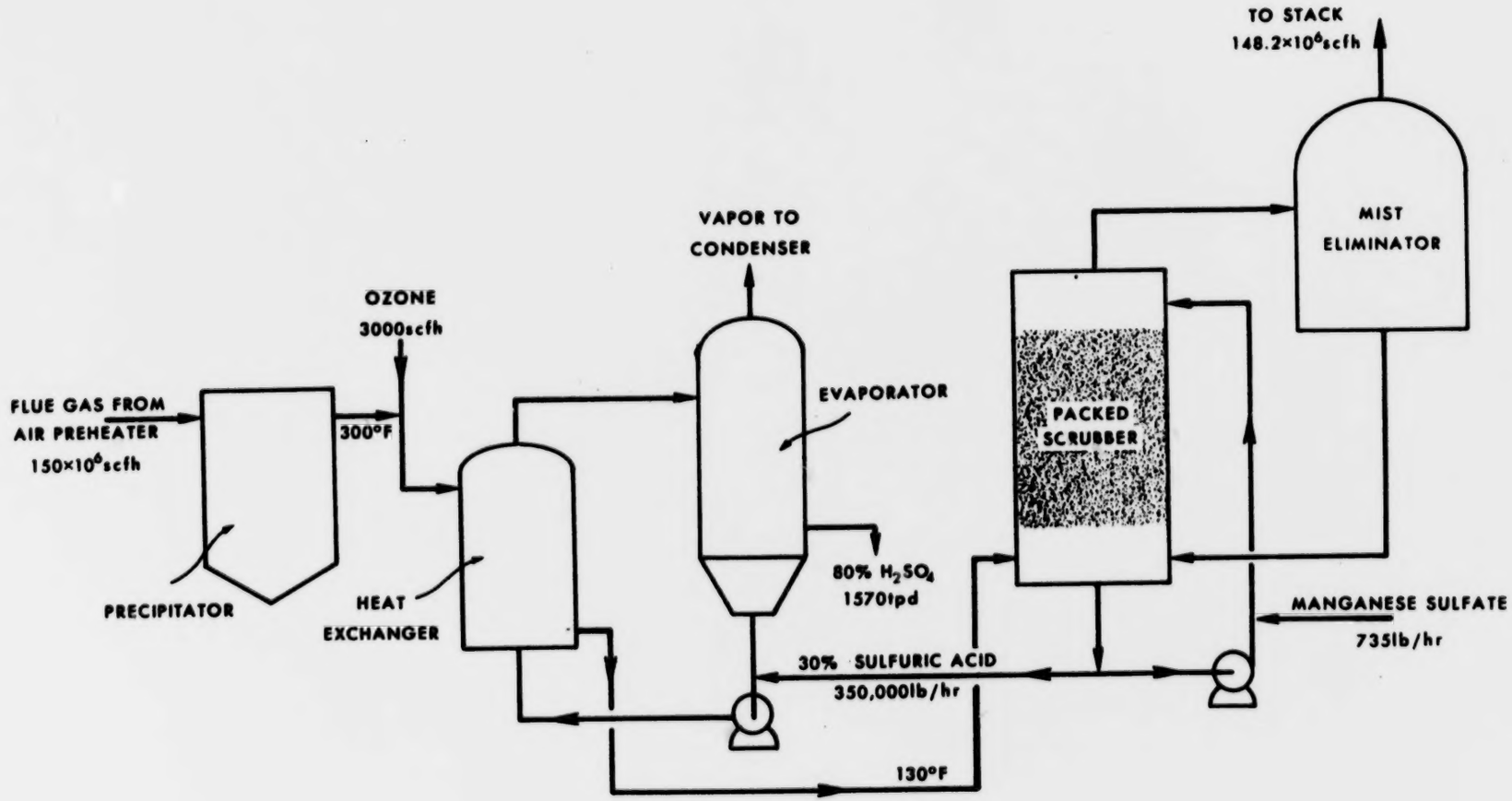


Figure 14. Flow Diagram of TVA Direct Sulfuric Acid Process

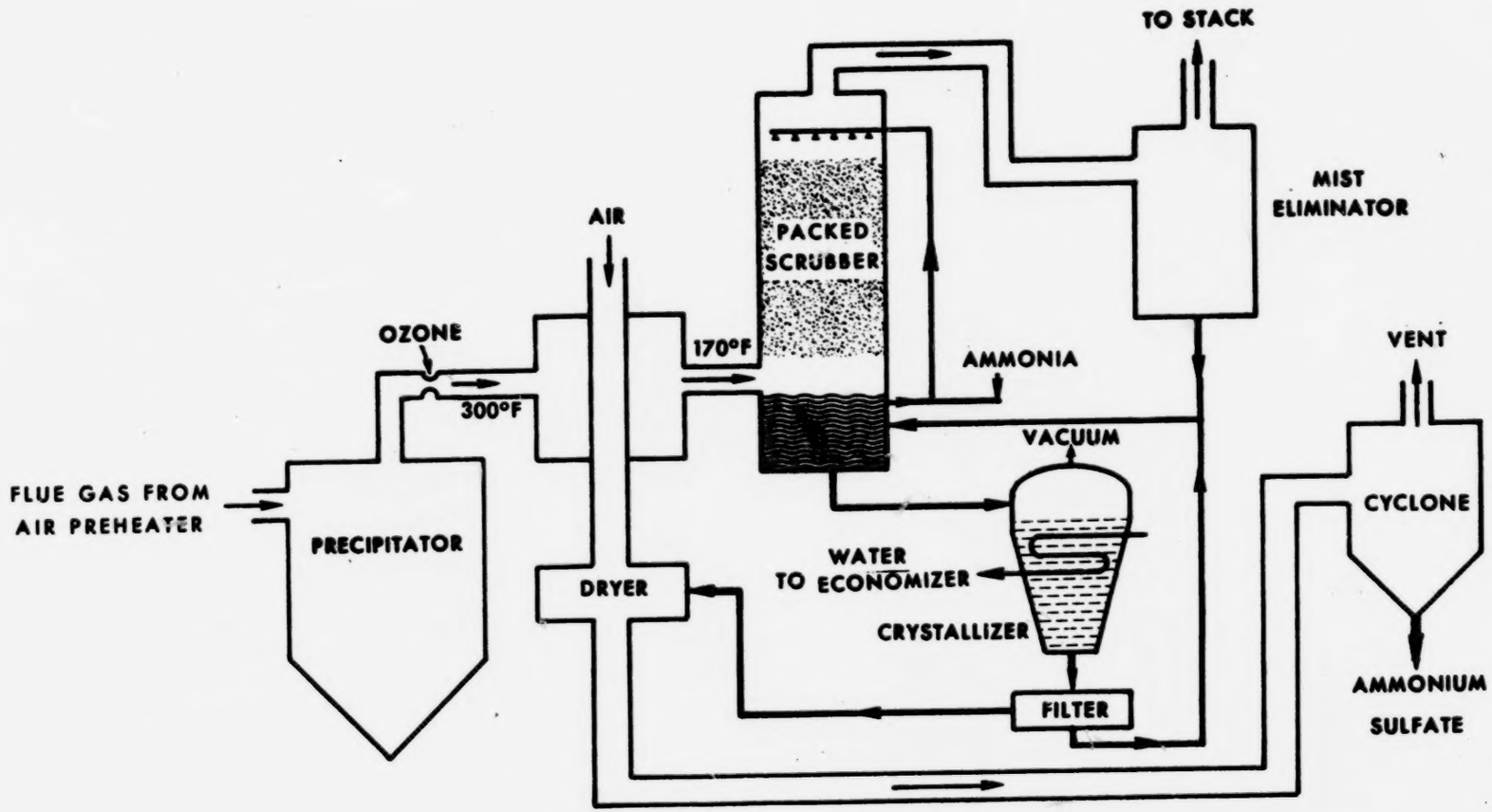


Figure 15. TVA Direct Ammonium Sulfate Process

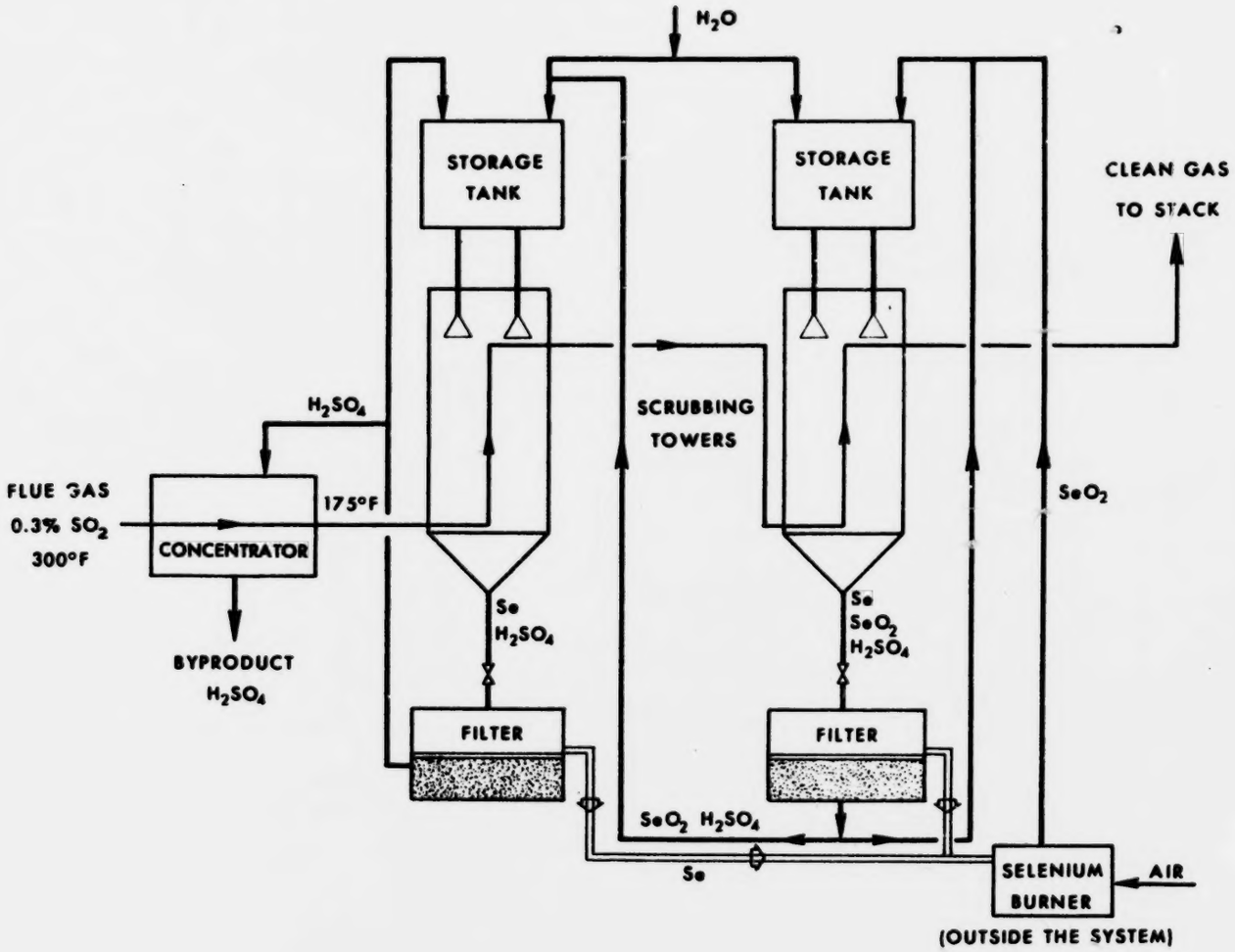


Figure 16. Nor Deutsche Affinerie Process for SO_2 Removal

b. Badische Anilin- and Soda-Fabrik Process (Ref. 128)

The Badische process, Figure 17, employs a single scrubbing tower, or a venturi scrubber, in which SO_2 is oxidized by selenium dioxide in a recirculating solution of selenous and sulfuric acids. The selenous acid concentration is maintained constant and in excess of stoichiometry with solid selenium continuously filtered out, reoxidized and reintroduced into the system from a side stream. In this process, residual selenium dioxide is reduced in the main product stream from the scrubber by reaction with another source of SO_2, e.g. roaster gas. The excess SO_2 in the gases from this step is vented into the incoming flue gas upstream of the removal system along with reoxidized selenium in vapor form.

The oxidation rate of SO_2 in the scrubbing liquor decreases with increasing concentration of H_2SO_4. However, the process may be operated in a multistage mode with each stage containing successively higher concentrations of H_2SO_4 in all of which SeO_2 is quite soluble. For example, in a two-stage process, the first stage liquor may be selenous acid and 30% H_2SO_4. The second stage would scrub the flue gas with H_2SeO_3 in 30% H_2SO_4. The H_2SO_4 produced in the first stage would be replaced by the 30% H_2SO_4 from the second stage. A three-stage system would run with first stage acid concentration at 70%, while the third stage would use 10% acid with an excess of selenous acid.

The basic difference in the two selenium processes lies in the mode of operation to produce a "clean", marketable product. The Nor Duetsche process strips selenous acid from the scrubbing liquor with excess SO_2 in the flue gas and concentrates the product acid with heat in the flue gas. The Badische process uses an outside source of SO_2 to strip selenous acid from the scrubbing liquor, with product concentration being dependent upon the number of scrubbing stages.

The selenium processes appear to be relatively simple. The oxi[illegible]t is recoverable, leading to low consumption and therefore minimum oxidant make-up. The production of marketable sulfuric acid is an advantage. Reduction in equipment size, compared with other wet processes, is indicated by the relatively high rate of oxidation of SO_2 by SeO_2.

The processes, however, also have some obvious disadvantages. Selenium is expensive and its oxides are highly toxic and corrosive. Removal of the elemental selenium from the system for reoxidation to SeO_2 and re-introducing it to the system could present a handling problem. Also, additional equipment and facilities would probably be required to wash and dry the selenium residue to remove absorbed sulfuric acid and separate the new SeO_2 from accumulated fly ash that was not retained by the dust collection system. Because the

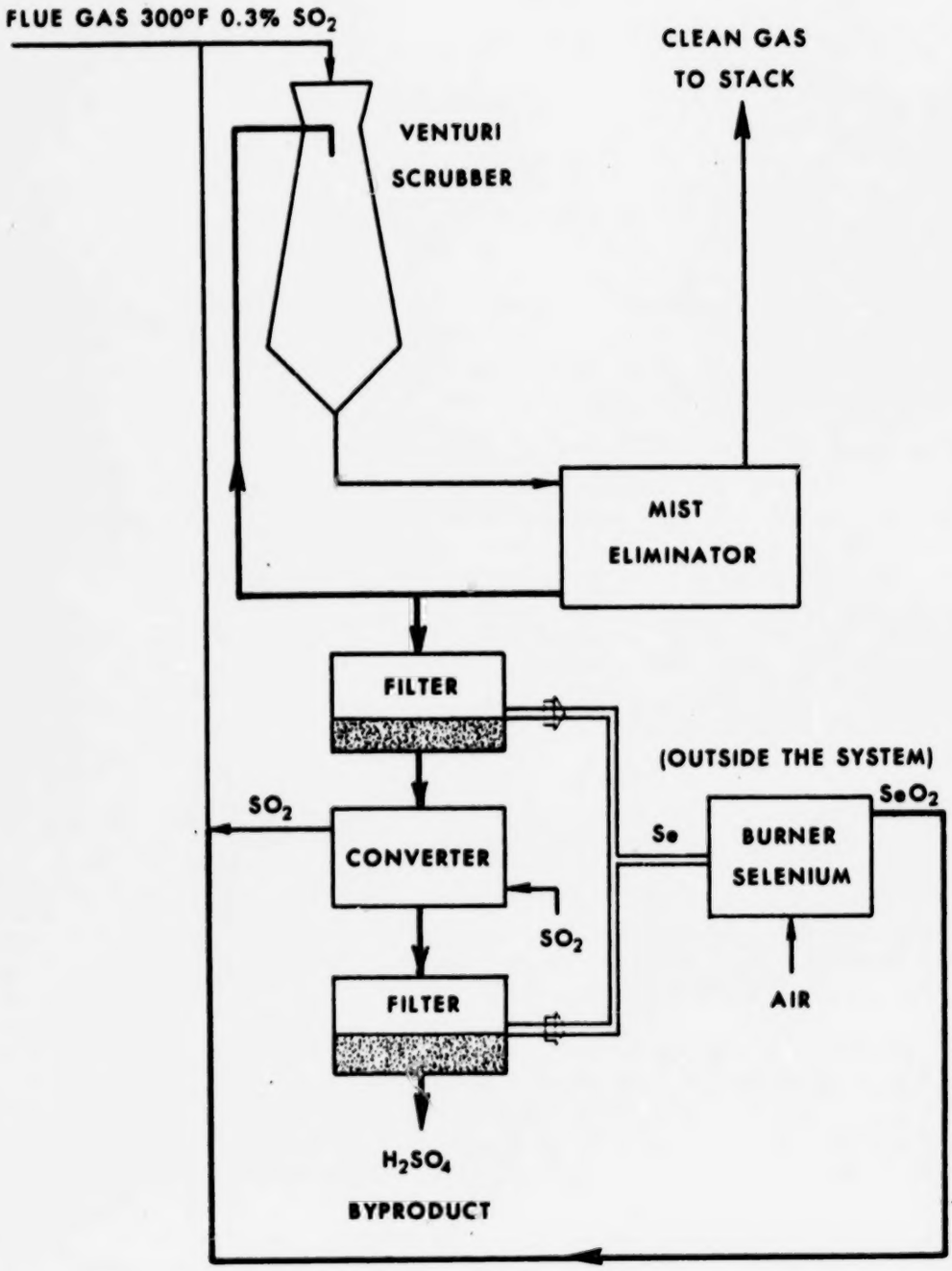


Figure 17. Badische Anilin- and Soda-Fabrik Process for SO_2 Removal

liquor and by-product is sulfuric acid, corrosion-resistant equipment would be required throughout the system. The temperature of the "cleaned" flue gas when exhausted to the atmospher is lower than needed to produce a high plume. However, since the reaction of Se with O_2 is exothermic, it may be possible to raise this temperature somewhat with the heat generated, by reoxidizing the elemental selenium.

Apparently, bench scale work has been done to evaluate some operating parameters. However, there is no knowledge that any pilot plant studies have been conducted, or are anticipated. This quite possibly may be attributed to the toxicity and cost of selenium.

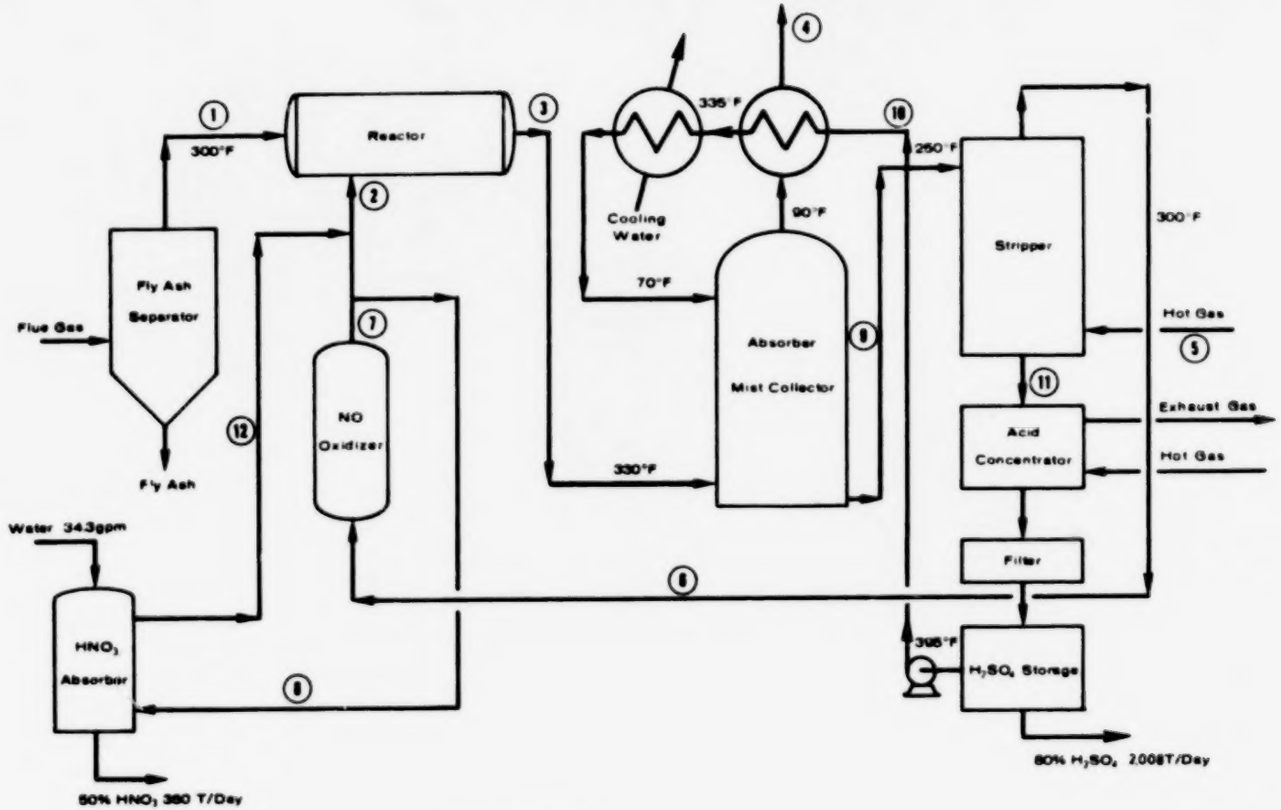
6. Modified Chamber Process

Tyco Laboratories, Waltham, Massachusetts, is studying a modified chamber-process approach to flue gas cleaning with NAPCA support. Since the oxides of nitrogen in flue gas are also objectionable, it is desirable to remove them along with the sulfur. Further, the oxides of nitrogen are capable of catalyzing the oxidation of sulfur dioxide. The obsolete chamber process utilized this principle to produce sulfuric acid commercially for a number of years.

In an early version of the Tyco process, Figure 18, flue gas at about 300°F enters the reactor where SO_2 is oxidized by nitrogen dioxide at a mole ratio of $3NO_2:NO:SO_2$. Retention time in the reactor is estimated at one to two seconds. Sulfur trioxide, nitrogen oxides, and water vapor are absorbed from the cooled reactor effluent in 80% sulfuric acid to form nitrosylsulfuric acid. Nitrogen oxides are stripped from the nitrosylsulfuric acid, sent to an oxidizing chamber where the proper mole ratio of $NO_2:NO$ is re-established, and then recycled to the converter. Since the entering flue gas contains some nitrogen oxides, there is a net accumulation of these in the system, and a side stream is used to make nitric acid, a second by-product of the process. Eighty percent sulfuric acid is obtained as by-product in a side stream from the absorber liquor.

Since the process is still in a very early stage of development, it is difficult to assess accurately the advantages and disadvantages. However, as initially described, the process clearly has one major advantage and one major disadvantage: it removes SO_2 and some NO_x at low temperature, but it requires the power station to burn 40% more fuel to supply high process heat requirements. Tyco is building a 10 c.f.m. pilot plant to investigate methods of lowering this prohibitively high heat load. Recent results indicate a more favorable heat balance.

Heat and material balances for an early version of the Tyco process are summarized in Figure 18. A later version of the process is discussed further in Volume II. In addition to general assumptions, the calculations here were based on the following assumptions:



Flue Gas Rate: 150 x 10^6 SCFH

Gas Flow, Weight %

Stream	1	2	3	4	5	6	7	8	9	10	11	12
N_2	70.18	62.06	68.77	74.00	70.18	61.75	61.75	61.75	--	--	--	64.99
CO_2	21.64	19.13	21.20	22.82	21.64	19.04	19.04	19.04	--	--	--	20.04
H_2O	4.40	10.34	5.42	0.36	4.40	10.29	10.29	10.29	22.84	20.00	22.29	10.83
O_2	3.07	1.54	2.63	2.82	3.07	2.51	1.65	1.65	--	--	--	1.73
SO_2	0.65	--	trace	trace	0.65	--	--	--	--	--	--	--
NO_x	0.06	--	--	--	0.06	--	--	--	--	--	--	--
NO_2	--	5.51	0.74	trace	--	3.88	6.36	6.36	0.58	--	--	--
NO	--	1.02	0.48	trace	--	2.53	0.91	0.91	0.38	--	--	2.41
H_2SO_4	--	--	0.76	--	--	--	--	--	76.20	80.00	77.71	--
Million lbs/hr	11.810	2.605	14.615	13.582	2.481	2.810	2.810	0.250	18.705	17.752	18.457	0.246

Figure 18. TYCO Modified Chamber Process

- SO_2 removal: 95%
- NO_x removal: 95%
- Molar ratio of NO_2: NO: SO_2 entering the reactor: 3:1:1
- Additional coal required for stripping gas: 21%
- Nitric acid concentration: 50%

7. Reversible Dry Absorbent Process

Callery Chemical Company, Division of Mine Safety Appliances Company, has considered a system for removing and concentrating the product SO_3 after conversion of the SO_2 in flue gas. A preliminary process design resulting from this NAPCA supported study is shown in Figure 19.

The exhaust from a catalytic converter is passed through a bed of absorbent (20 wt % of Na_2SO_4 on inert support) where product SO_3 is absorbed (forming $Na_2S_2O_7$). Exhausted absorbent is regenerated with hot gas which releases the SO_2. The regenerant stream containing 20 vol % SO_3 is fed to an acid absorption column to produce 100% acid or oleum.

For a fixed bed system, four absorption columns are required to permit adequate cycle timing, as illustrated by the following:

ABSORBER NUMBER

1	2	3	4
15 min. abs.	---	---	---
15 min. des.	15 min. abs.	---	---
15 min. des.	15 min. des.	15 min. abs.	---
15 min. cool.	15 min. des.	15 min. des.	15 min. des.

This process is described in greater detail in Volume II.

Advantages of the process include the production of 100% acid, and elimination of the need for corrosion resistant equipment in the flue gas stream.

Disadvantages include effects of thermal cycling on absorbent, unknown absorbent attrition rate, and early development status.

Flue Gas Rate: 150 x 10^6 SCFH
Gas Flow, Wt. %

Stream	A	B	C	D	E	F	G
N_2	70.18	70.69	70.18	41.60	70.19	-	70.69
CO_2	21.64	21.79	21.64	12.82	21.64	-	21.79
H_2O	4.48	4.45	4.40	2.61	4.40	0.5	4.45
O_2	2.93	2.96	3.07	1.82	3.08	-	2.95
SO_2	0.06	0.06	0.65	0.38	0.64	-	0.07
SO_3	0.73	Trace	-	40.74	Trace	-	Trace
NO_x	0.06	0.05	0.06	0.03	0.05	-	0.05
H_2SO_4	-	-	-	-	-	99.5	-
lbs/hr (10^4)	11.810	11.729	0.118	0.199	0.118	0.100	11.847

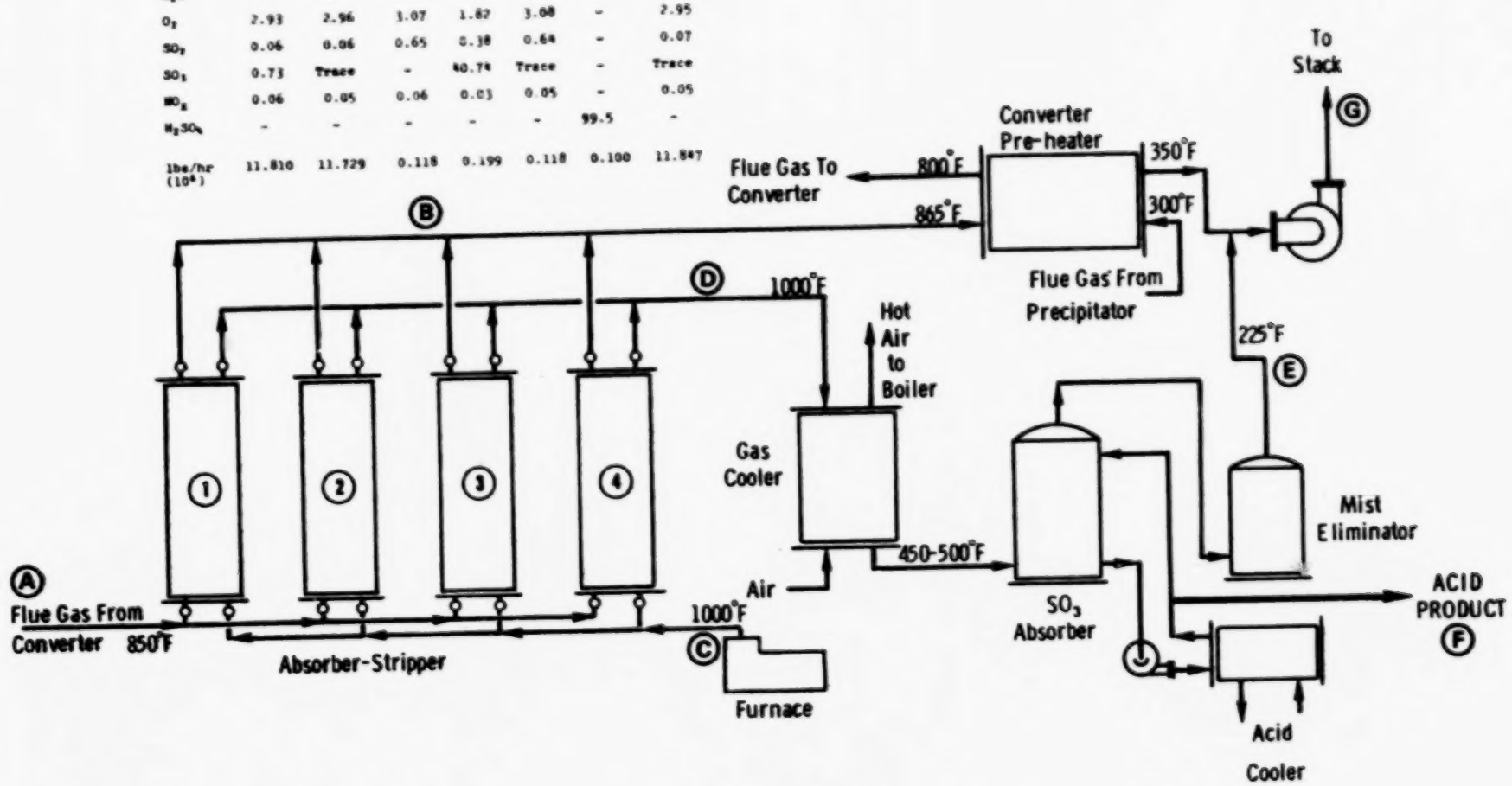


Figure 19. Callery Dry Absorbent Process

8. Process Cost Estimates

Table 10 summarizes the capital requirements and operating costs for the 7 processes. Capital requirements for Sulfacid and TVA direct acid process were based on limited literature data. Estimates for Hitachi, TVA-ammonium sulfate, selenium and Tyco processes are not included because of insufficient design information on these processes. Preliminary capital requirement estimates and operating costs were based on the following assumptions:

General:

- Flue gas rate - 2.5 MM SCFM
- Size of power plant - 1400 MW
- Flue gas analysis:

Component	% by Volume
N_2	74.9
CO_2	14.7
H_2O	7.25
O_2	2.8
SO_2	0.3
NO_x	0.05
Fly Ash	0.2 (by weight)

- Coal required - 580 tons/hr
- Operating factor - 330 days/yr @ 100% capacity
- Direct labor - $3.00/hr
- Supervision - $7,800 and $12,000 annually for first-line supervisors and area superintendents, respectively
- Maintenance - 5% of the fixed capital investment
- Plant supplies - 15% of the maintenance cost
- Utilities:

  a) steam - 50¢/1000 lbs
  b) electricity - $0.006/Kw-hr

Table 10

Capital Requirements and Operating Costs
for SO_2 Oxidation Processes
(for capital cost breakdown, see Appendix IV)

Process	Capital Requirement		Operating Cost			By Product
	Dollars	$/KW	$/Yr.	$/Ton of Coal	Mills/KWH	
Monsanto-Penelec[1]	37,489,000	26.77	10,643,000	2.32	0.96	70 to 80% sulfuric acid
Monsanto-Penelec[2]	34,067,000	24.33	9,506,000	2.07	0.86	70 to 80% sulfuric acid
Kiyora-T.I.T.[1]	25,889,000	18.49	16,568,000	3.60	1.49	Ammonium sulfate
Kiyora-T.I.T.[2]	22,473,000	16.05	15,425,000	3.36	1.39	Ammonium sulfate
Reinluft[1]	31,460,000	22.47	13,531,000	2.95	1.22	98% sulfuric acid
Sulfacid[1]	67,925,000	48.51	24,320,000	5.29	2.19	93% sulfuric acid
Mitsubishi[1]	22,869,000	16.33	16,450,000	3.58	1.48	Ammonium sulfate
T.V.A.-Direct Acid[1]	61,600,000	44.00	21,536,000	4.69	1.94	80% sulfuric acid
Callery Dry Absorbant[3]	16,830,000	12.02	4,724,150	1.03	0.43	99% sulfuric acid

1. low temperature effluent (about 300°F) from existing power plant

2. high temperature effluent (about 850°F) from new power plant

3. low temperature effluent from existing power plant, including catalytic converter

c) water

raw (untreated)	10¢/1000 gal
process (treated)	25¢/1000 gal
recirculated cooling tower	5¢/1000 gal

d) compressed air - 5¢/1000CF

- Payroll burden - 20% of direct labor and supervision
- Plant overhead - 50% of labor, maintenance and supplies
- Depreciation - 10% of the fixed capital investment
- Taxes - 2% of the fixed capital investment
- Insurance - 1% of the fixed capital investment
- Working capital - 10% of the fixed capital investment.

Monsanto-Penelec Process

- SO_2 conversion: 90%
- SO_3 recovered as H_2SO_4: 95%
- Contact time: 0.3 sec.
- Pressure drop across catalyst bed: 4 in H_2O/ft of depth
- Vanadium catalyst life: 5 years
- Vanadium catalyst cost: $1.45/liter
- Density of vanadium catalyst: 36 lb/ft^3

Kiyoura - T.I.T. Process

Same as for the Monsanto-Penelec process, plus the following:

- Ammonia cost: $60.00/ton
- Size of $(NH_4)_2 SO_4$ particles: 1-3 microns,
  Aggregate size: above 100 microns

Reinluft Process

- Adsorption of SO_2 by carbon: 0.1 lb SO_2/lb carbon
- Carbon losses:

  Chemical Reaction: 0.2 lb/lb of sulfur
  Attrition: 0.2 lb/lb of sulfur

- SO_2 recovered: 95%
- SO_2 concentration in product gas: 25%
- Conversion efficiency for sulfuric acid plant: 96%

- Residence time in adsorber: 1 sec.
- Linear velocity in adsorber: 100 ft/sec
- Adsorbent carbon cost: $80.00/ton
- Vanadium catalyst cost for sulfuric acid plant: $1.45/liter
- Vanadium catalyst life for sulfuric acid plant: 5 years

Sulfacid Process

- SO_2 conversion: 90%
- Contact time: 10 sec
- Linear velocity in reactor: 100 ft/sec
- Catalyst life: 3 years
- Cost of active coal: $220.00/ton
- Density of active coal: 22 lb/ft^3

Mitsubishi Process

- SO_2 conversion: 90%
- Absorbent used: 200g/cu m
- Cyclone efficiency: 90%
- Amount of water in slurry: 70%
- Residence time in absorber: 1 sec
- Linear velocity in absorber: 150 ft/sec
- Absorbent loss due to attrition: 0.1 lb/lb of sulfur
- Ammonia cost: $60.00/ton
- Absorbent cost: $144.00/ton

TVA-direct sulfuric acid

- SO_2 conversion: 90%
- Amount of $MnSO_4$: 0.3 lb $MnSO_4$/100 lbs water
- Amount of ozone injected in flue gas: 20 P.P.M.
- Residence time in packed scrubber: 10 sec
- Linear velocity in packed scrubber: 70 ft/sec
- $MnSO_4$ cost: $95.00/ton

Callery Process

SO_2 converted to SO_3 - 90%

Amount of Na_2SO_4 in total absorbant - 20% (by weight)

100% absorption efficiency, i.e., stoichiometric absorption, for 15 minutes

Vanadium catalyst cost - $1.45/liter

Vanadium catalyst life - 5 years

Cost of Na_2SO_4 - $30.00/ton

Cost of Coal - $4.00/ton

Tables 11 through 19 summarize the preliminary cost estimates of major equipment for the seven processes. As it is possible to have low and high temperature effluent feed to Monsanto-Penelec and Kiyoura-T.I.T. processes, cost estimates at both conditions were made for these two processes. The other processes were based on low temperature effluent (300°F). Fixed capital costs were estimated after application of Lang's factors of 4.74 for fluid process plants and 3.63 for solid/fluid process plants. Working capital was set at 10% of the fixed capital investment for estimating the total investment.

The operating costs of Monsanto-Penelec, Kiyoura-T.I.T., Reinluft, Callery, Sulfacid, Mitsubishi and T.V.A.-Direct Acid processes were estimated. Tables 11 through 19 summarize these estimated operating costs. The credit for by-product sulfur, sulfuric acid or ammonium sulfate has a major effect on the net operating costs. Since the prices of these by-products fluctuate, Figures 19 to 27 present the relationship of sales value of by-product to the net operating cost. Capital costs are summarized in Appendix IV.

9. Comparative Evaluation of Flue Gas Treatment Processes

Although a number of processes have been described, only a few have been well-developed, and, even among these, not all are worthy of further consideration. The preliminary cost estimates have a good deal to say in this respect. It remains to be pointed out those approaches that might well be pursued and those that should not, in view of current information.

The wet manganese-based processes do not appear to hold promise. The wet methods studied by TVA display no characteristics to suggest further study. The dry manganese oxide, non-catalytic process of Mitsubishi produces ammonium sulfate, which, it seems, can be produced as efficiently by the Kiyoura catalytic process. Further, the Mitsubishi process can produce only ammonium sulfate (or an alkali sulfate), whereas, the Kiyoura process can produce either this product or sulfuric acid. The one salient advantage of the Mitsubishi process is its adaptability to low temperature stack gas, i.e. existing power stations.

In this latter respect, the carbon processes are tempting to further consideration. However, associated with the dry carbon techniques are two grave obstacles: 1) the tenacious bond between carbon and product sulfuric acid, and 2) the instability of carbon in the presence of the relatively large amount of residual oxygen in the flue gas. Both disadvantages are manifest in the Reinluft process, which, finally, is an adsorption technique producing SO in a concentrated stream. In attempting to circumvent these obstacles, the wet carbon processes have introduced a new set of problems which limits their potential to small and specialized installations where long retention times in adsorbers and weak acid product may not count so heavily. Otherwise, there appears to be no basis for further consideration of carbon.

It has already been indicated that the selenium dioxide reaction with sulfur dioxide is not catalytic but stoichiometric. The health hazard, associated with selenium compounds, has also been noted. Nevertheless, selenium dioxide presents some interesting aspects for potential treatment processes. For example (a) Does the reaction proceed at a satisfactory rate in the vapor phase? and (b) Since there is excess oxygen in the flue gas, in a bed of solid selenium dioxide, could the following reactions be made to occur concurrently through the bed?

$$2\ SO_2 + SeO_2 \longrightarrow 2\ SO_3 + Se \qquad (29)$$

$$Se + O_2 \longrightarrow SeO_2 \qquad (30)$$

From an academic viewpoint, if the reaction rates are good enough, the concept under (b) offers interesting process possibilities for low temperature application.

The Tyco modified chamber-process approach to flue gas SO_2 oxidation presents a number of problems. Again, this process offers ready adaptability to low temperature operation - its major advantage. However, this process is under separate investigation by NAPCA.

Finally, there are the vanadium-based processes. In producing ammonium sulfate, Kiyoura obviates the high costs of corrosion resistant materials of construction. On the other hand, in this country, the product would present a considerable disposal problem.

Except for some proprietary engineering and operational differences we might say that there is only one vanadium process, since either of the two described could produce sulfuric acid or ammonium sulfate. The greatest advantage of the vanadia process is its simplicity; the major disadvantage is its poorer operating economics when applied to low temperature effluent (existing plants). Further, the Monsanto-Penelec version of the vanadia process affords, with minor modifications, the same opportunity for NO_x removal as the Tyco (modified chamber) process.

The Callery reversible dry absorbent process is not <u>per se</u> an SO_2 removal process, as it depends upon a prior step to convert SO_2 to SO_3. However, it is presented here because of the apparent effect it has on improving the economics of a process like the Monsanto-Penelec process (see Table 21). It also points up the potential value of a process that could sorb SO_2 directly from flue gas and desorb a concentrated stream of SO_2 to a contact converter for acid production or to a Claus reactor for elemental sulfur production.

Table 11

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @100% Capacity

Category: Existing Power Plant (Low Temperature Effluent)

Name of Process Monsanto-Penelec Flue Gas Rate 2.5 MMSCFM

MW 1400

Fixed Capital Cost $34,081,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	250,000	2.35
2.	Direct Labor	105,000	0.98
3.	Supervision	31,200	0.30
4.	Maintenance, 5% of Fixed Capital	1,700,000	15.98
5.	Supplies, 15% of Maintenance	255,000	2.39
6.	Utilities	2,800,000	26.30
7.	Other		
8.	TOTAL DIRECT COST	5,141,200	48.30
9.	Payroll Burden, 20% of 2 & 3	27,200	0.26
10.	Plant Overhead, 50% of 2, 3, 4 and 5	1,045,600	9.75
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	1,072,800	10.01
15.	Depreciation, 10 % Fixed Capital/Yr.	3,408,100	32.10
16.	Taxes, 2% of Fixed Capital	680,000	6.38
17.	Insurance, 1% of Fixed Capital	341,000	3.21
18.	Other		
19.	TOTAL FIXED COST	4,429,100	41.69
20.	TOTAL OPERATING COST	10,643,100	100.00
21.	COST: $/Ton of Coal 2.32 Mill/kwh 0.96		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal _____ Mill/kwh _____		

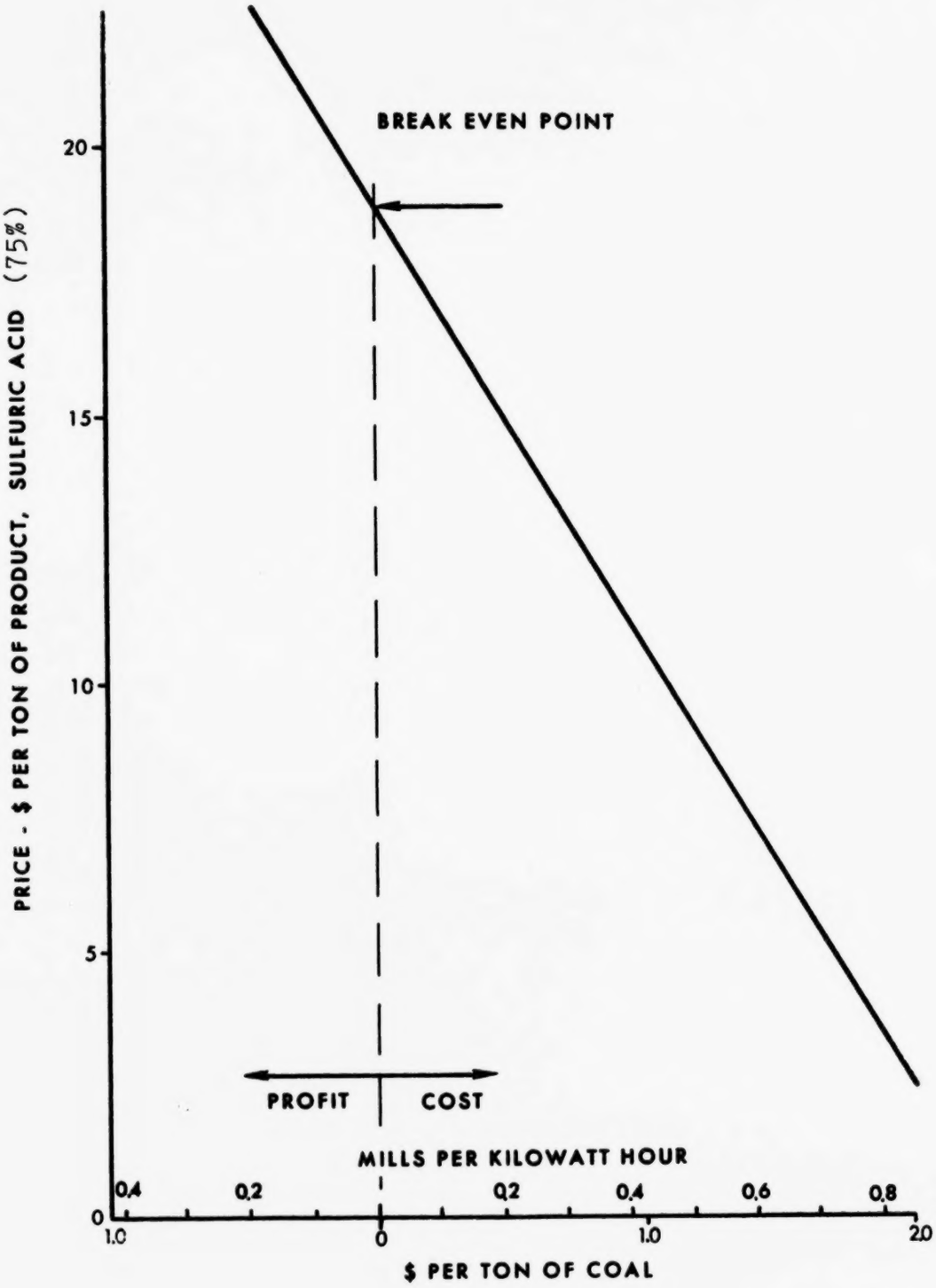


Figure 19. Effect of Product Credit on Operating Cost of Monsanto-Penelec Process (Existing Plant)

Table 12

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @100% Capacity

Category: New Power Plant (High Temperature Effluent)

Name of Process Monsanto-Penelec Flue Gas Rate 2.5 MMSCFM

MW 1400

Fixed Capital Cost $30,970,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	250,000	2.63
2.	Direct Labor	105,000	1.11
3.	Supervision	31,200	0.33
4.	Maintenance, 5% of Fixed Capital	1,550,000	16.30
5.	Supplies, 15% of Maintenance	232,000	2.44
6.	Utilities	2,325,000	24.45
7.	Other		
8.	TOTAL DIRECT COST	4,493,200	47.26
9.	Payroll Burden, 20% of 2 & 3	27,200	0.29
10.	Plant Overhead, 50% of 2, 3, 4 and 5	959,100	10.09
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	986,300	10.38
15.	Depreciation, 16 % Fixed Capital/Yr.	3,097,000	32.58
16.	Taxes, 2% of Fixed Capital	620,000	6.52
17.	Insurance, 1% of Fixed Capital	309,700	3.26
18.	Other		
19.	TOTAL FIXED COST	4,026,100	42.36
20.	TOTAL OPERATING COST	9,505,600	100.00
21.	COST: $/Ton of Coal 2.07 Mill/kwh 0.86		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal _____ Mill/kwh _____		

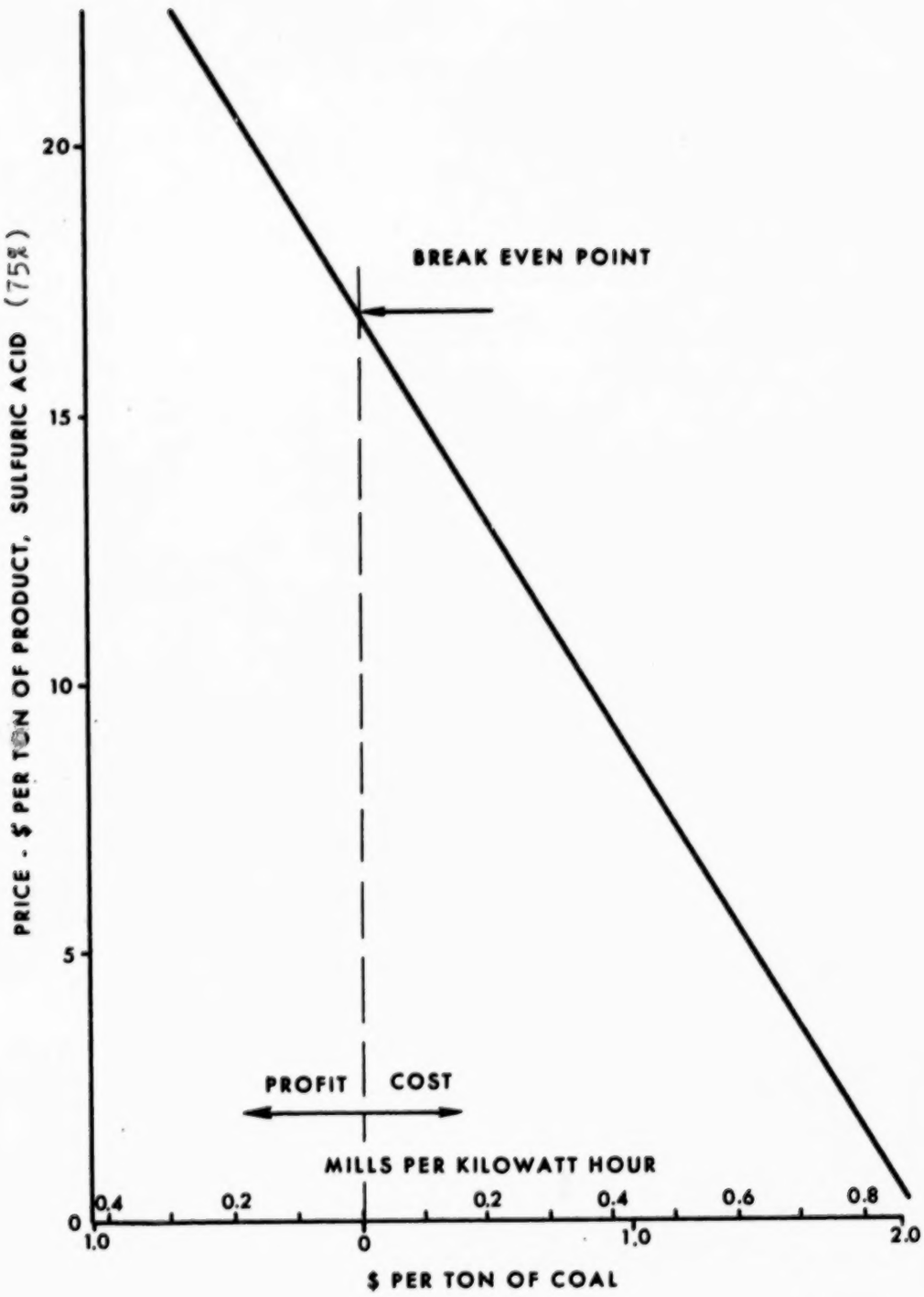


Figure 20. Effect of Product Credit on Operating Cost of Monsanto-Penelec Process (new Plant)

Table 13

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @100% Capacity

Category: Existing Power Plant (Low Temperature Effluent)

Name of Process Kiyoura - T.I.T. Flue Gas Rate 2.5 MMSCFM

MW 1400

Fixed Capital Cost $23,535,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	8,450,000	51.00
2.	Direct Labor	105,000	0.64
3.	Supervision	31,200	0.19
4.	Maintenance, 5% of Fixed Capital	1,175,000	7.09
5.	Supplies, 15% of Maintenance	176,000	1.06
6.	Utilities	2,800,000	16.90
7.	Other		
8.	TOTAL DIRECT COST	12,737,200	76.88
9.	Payroll Burden, 20% of 2 & 3	27,200	0.17
10.	Plant Overhead, 50% of 2, 3, 4 and 5	743,600	4.48
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	770,800	4.65
15.	Depreciation, 10 % Fixed Capital/Yr.	2,353,500	14.21
16.	Taxes, 2% of Fixed Capital	470,700	2.84
17.	Insurance, 1% of Fixed Capital	235,350	1.42
18.	Other		
19.	TOTAL FIXED COST	3,059,550	18.47
20.	TOTAL OPERATING COST	16,567,550	100.00
21.	COST: $/Ton of Coal 3.60 Mill/kwh 1.49		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal Mill/kwh		

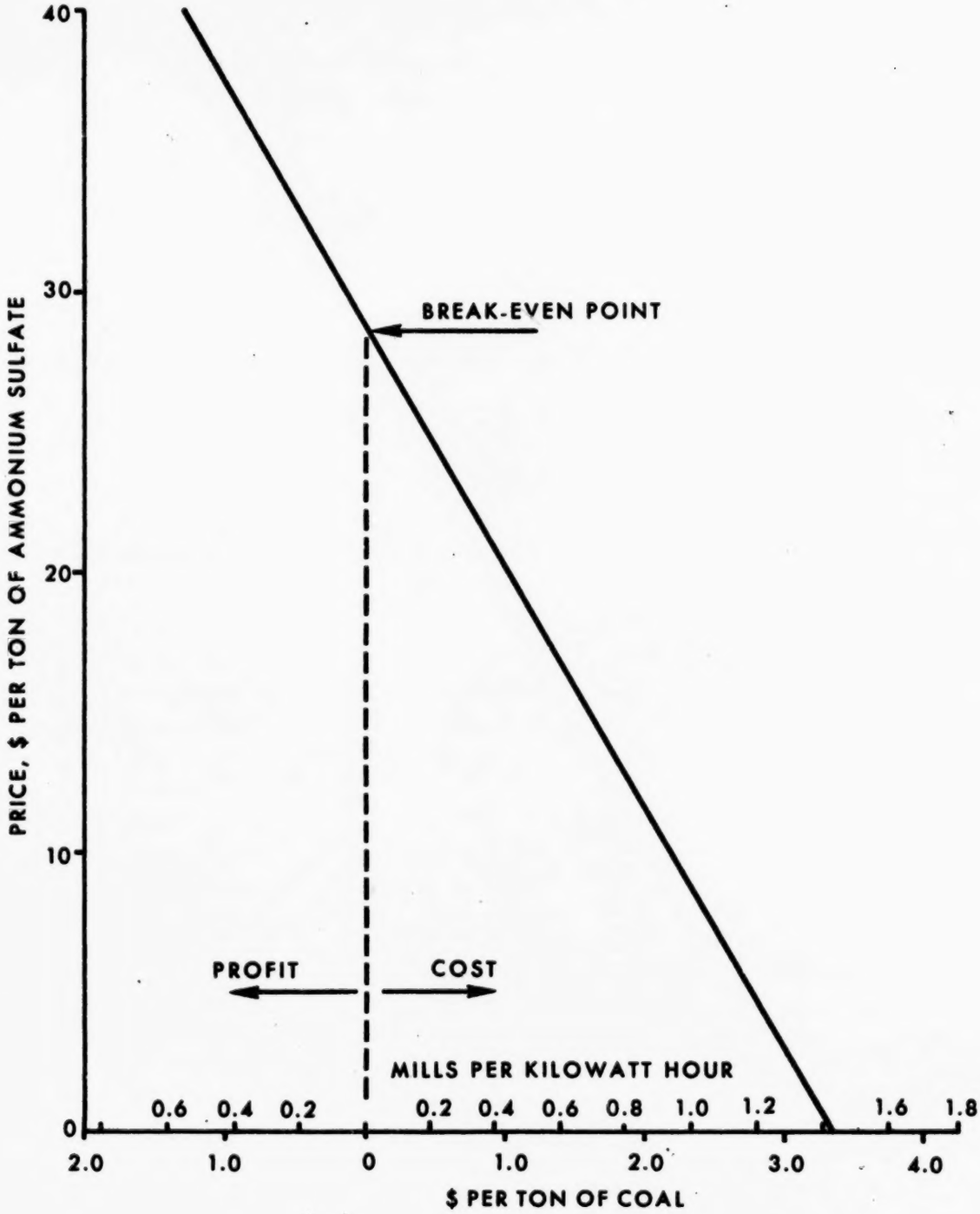


Figure 21. Effect of Product Credit on Operating Cost of Kiyoura-T.I.T. Process (Existing Plant)

Table 14

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @100% Capacity

Category: New Power Plant (High Temperature Effluent)

Name of Process Kiyoura - T.I.T. Flue Gas Rate 2.5 MMSCFM

MW 1400

Fixed Capital Cost $20,430,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	8,450,000	54.78
2.	Direct Labor	105,000	0.68
3.	Supervision	31,200	0.20
4.	Maintenance, 5% of Fixed Capital	1,021,500	6.62
5.	Supplies, 15% of Maintenance	153,300	0.98
6.	Utilities	2,325,000	15.10
7.	Other		
8.	TOTAL DIRECT COST	12,086,000	78.36
9.	Payroll Burden, 20% of 2 & 3	27,200	0.17
10.	Plant Overhead, 50% of 2, 3, 4 and 5	655,500	4.25
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	682,700	4.42
15.	Depreciation, 10 % Fixed Capital/Yr.	2,043,000	13.25
16.	Taxes, 2% of Fixed Capital	408,600	2.65
17.	Insurance, 1% of Fixed Capital	204,300	1.32
18.	Other		
19.	TOTAL FIXED COST	2,655,900	17.22
20.	TOTAL OPERATING COST	15,424,600	100.00
21.	COST: $/Ton of Coal 3.36 Mill/kwh 1.39		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal Mill/kwh		

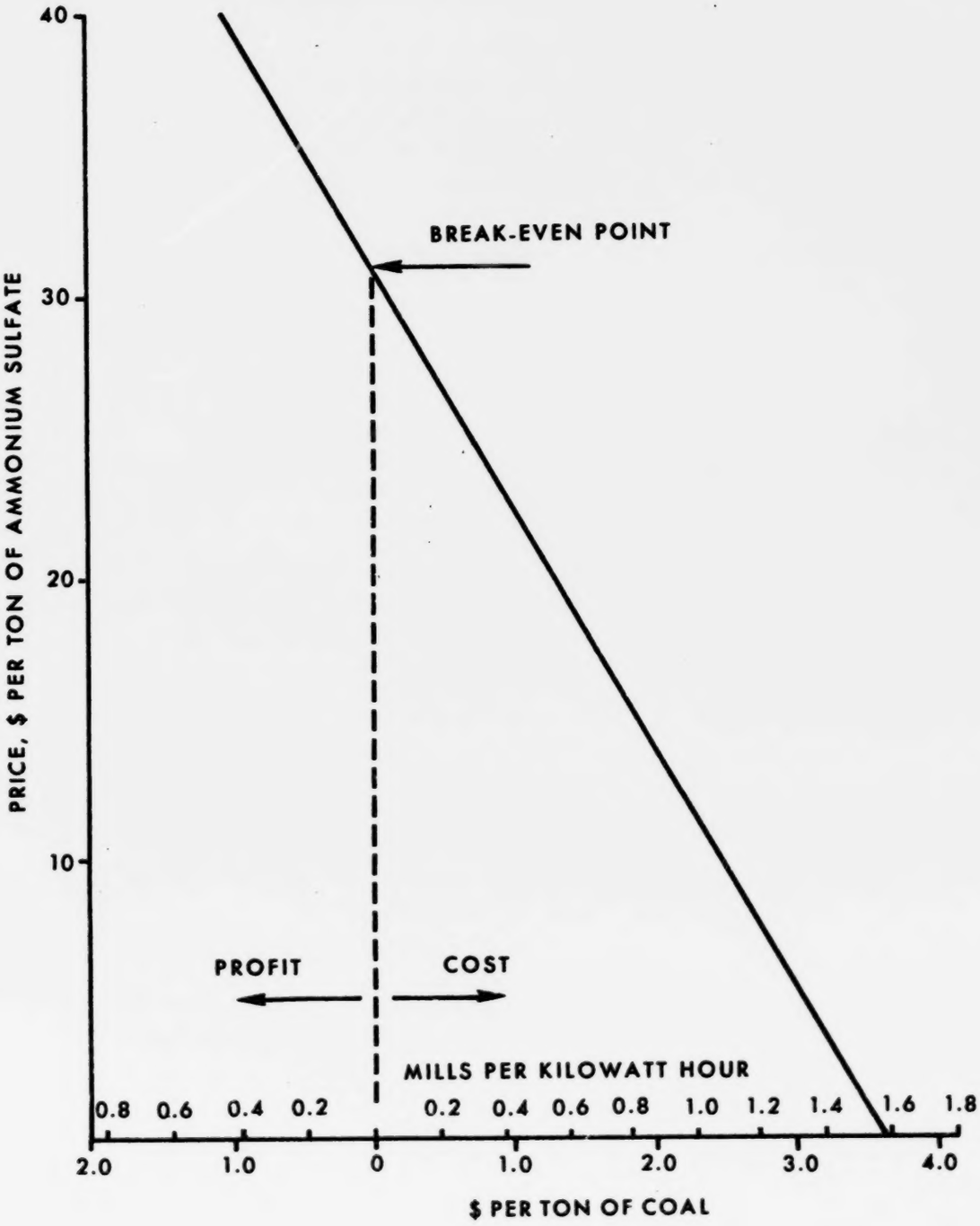


Figure 22. Effect of Product Credit on Operating Cost of Kiyoura-T.I.T. Process (New Plant)

Table 15

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @100% Capacity

Category: Low Temperature Effluent

Name of Process Reinluft Process Flue Gas Rate 2.5 MMSCFM

MW 1400

Fixed Capital Cost $28,600,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	4,687,000	34.64
2.	Direct Labor	315,000	2.33
3.	Supervision	31,200	0.23
4.	Maintenance, 5% of Fixed Capital	1,430,000	10.56
5.	Supplies, 15% of Maintenance	214,500	1.59
6.	Utilities	2,070,200	15.30
7.	Other		
8.	TOTAL DIRECT COST	8,747,900	64.65
9.	Payroll Burden, 20% of 2 & 3	69,300	0.51
10.	Plant Overhead, 50% of 2, 3, 4 and 5	995,400	7.36
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	1,064,700	7.87
15.	Depreciation, 10 % Fixed Capital/Yr.	2,860,000	21.14
16.	Taxes, 2% of Fixed Capital	572,000	4.23
17.	Insurance, 1% of Fixed Capital	286,000	2.11
18.	Other		
19.	TOTAL FIXED COST	3,718,000	27.48
20.	TOTAL OPERATING COST	13,530,600	
21.	COST: $/Ton of Coal 2.95 Mill/kwh 1.22		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal _____ Mill/kwh _____		

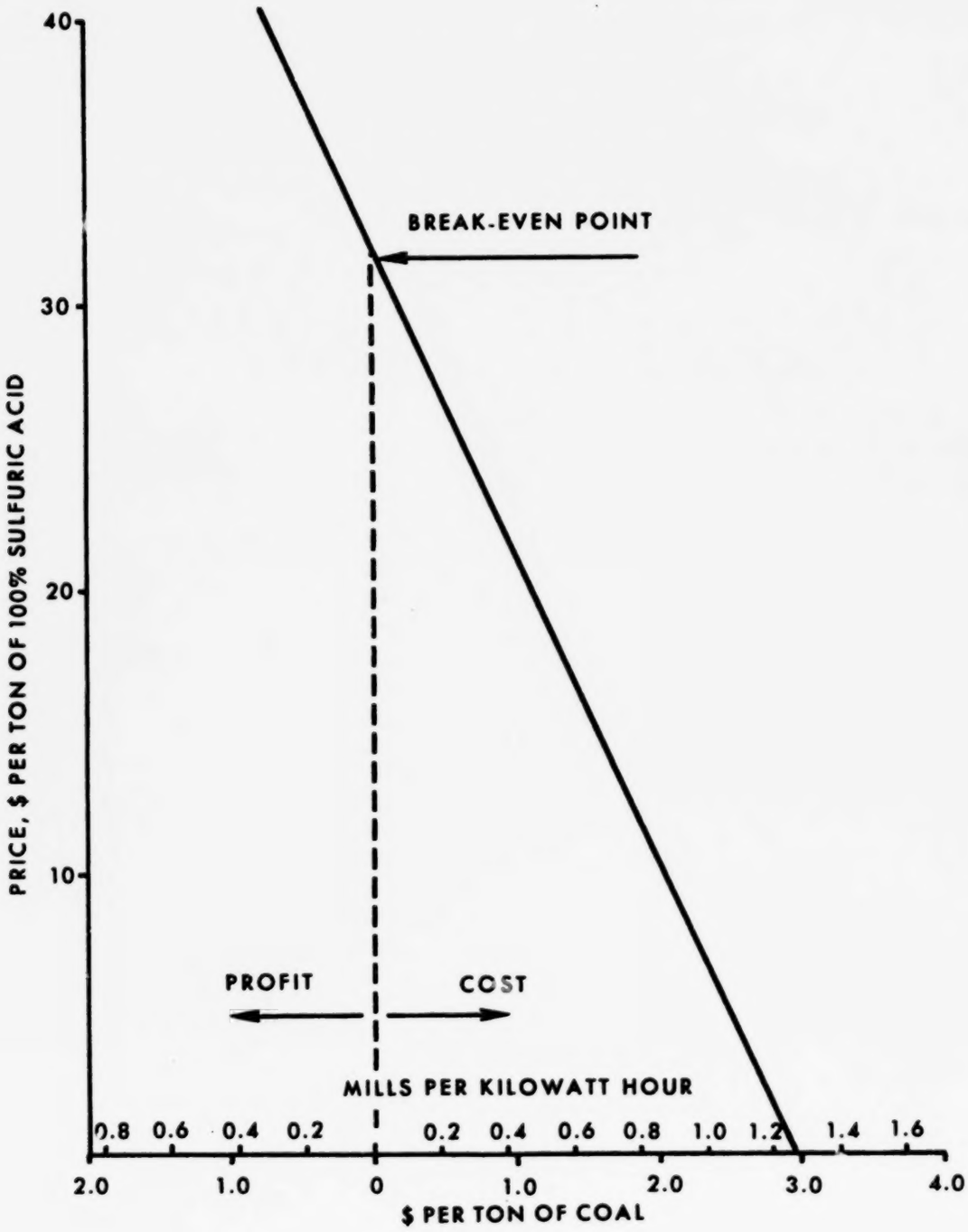


Figure 23. Effect of Product Credit on Operating Cost of Reinluft Process

Table 16

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @100% Capacity

Category: Low Temperature Effluent

Name of Process Sulfacid Process Flue Gas Rate 2.5 MMSCFM

MW 1,400

Fixed Capital Cost 61,750,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	378,000	1.56
2.	Direct Labor	105,000	0.43
3.	Supervision	31,200	0.12
4.	Maintenance, 5% of Fixed Capital	3,087,500	12.69
5.	Supplies, 15% of Maintenance	463,200	1.91
6.	Utilities	10,356,600	42.59
7.	Other		
8.	TOTAL DIRECT COST	14,421,500	59.30
9.	Payroll Burden, 20% of 2 & 3	27,300	0.11
10.	Plant Overhead, 50% of 2, 3, 4 and 5	1,843,500	7.59
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	1,870,800	7.70
15.	Depreciation, 10 % Fixed Capital/Yr.	6,175,000	25.39
16.	Taxes, 2% of Fixed Capital	1,235,000	5.08
17.	Insurance, 1% of Fixed Capital	617,500	2.53
18.	Other		
19.	TOTAL FIXED COST	8,027,500	33.00
20.	TOTAL OPERATING COST	24,319,800	100.00
21.	COST: $/Ton of Coal 5.29; Mill/kwh 2.19		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal ____; Mill/kwh ____		

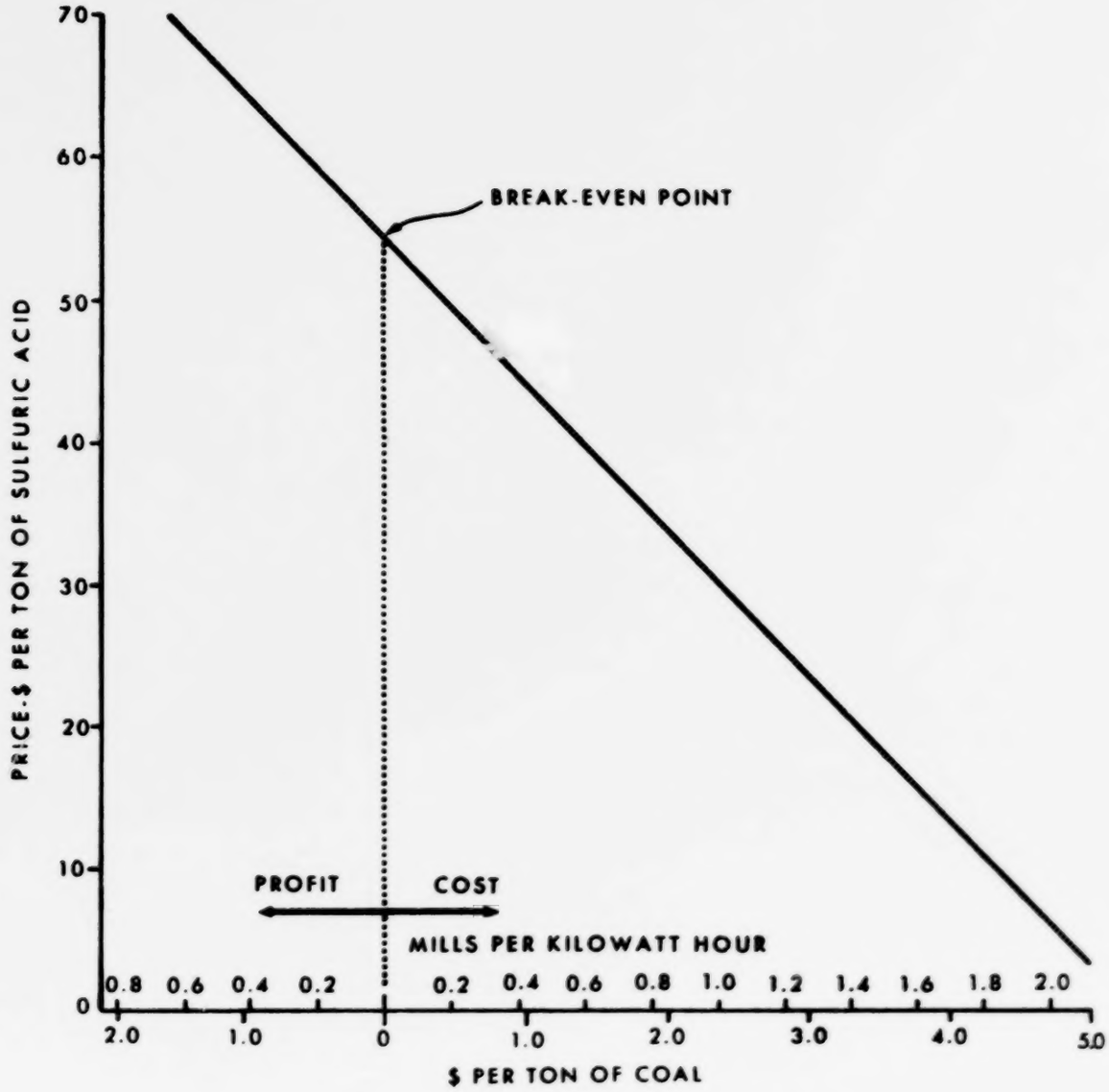


Figure 24. Effect of Product Credit on Operating Cost of Reinluft Process

Table 17

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @100% Capacity

Category: Low Temperature Effluent

Name of Process Mitsubishi Process Flue Gas Rate 2.5 MMSCFM

MW 1,400

Fixed Capital Cost $20,790,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	10,765,000	65.46
2.	Direct Labor	315,000	1.91
3.	Supervision	31,200	0.18
4.	Maintenance, 5% of Fixed Capital	1,039,500	6.32
5.	Supplies, 15% of Maintenance	156,000	0.94
6.	Utilities	600,000	3.65
7.	Other		
8.	TOTAL DIRECT COST	12,906,700	78.46
9.	Payroll Burden, 20% of 2 & 3	69,300	0.42
10.	Plant Overhead, 50% of 2, 3, 4 and 5	770,900	4.68
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	840,200	5.10
15.	Depreciation, 10 % Fixed Capital/Yr.	2,079,000	12.65
16.	Taxes, 2% of Fixed Capital	415,800	2.53
17.	Insurance, 1% of Fixed Capital	208,000	1.26
18.	Other		
19.	TOTAL FIXED COST	2,702,800	16.44
20.	TOTAL OPERATING COST	16,449,700	100.00
21.	COST: $/Ton of Coal 3.58; Mill/kwh 1.48		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal ____; Mill/kwh ____		

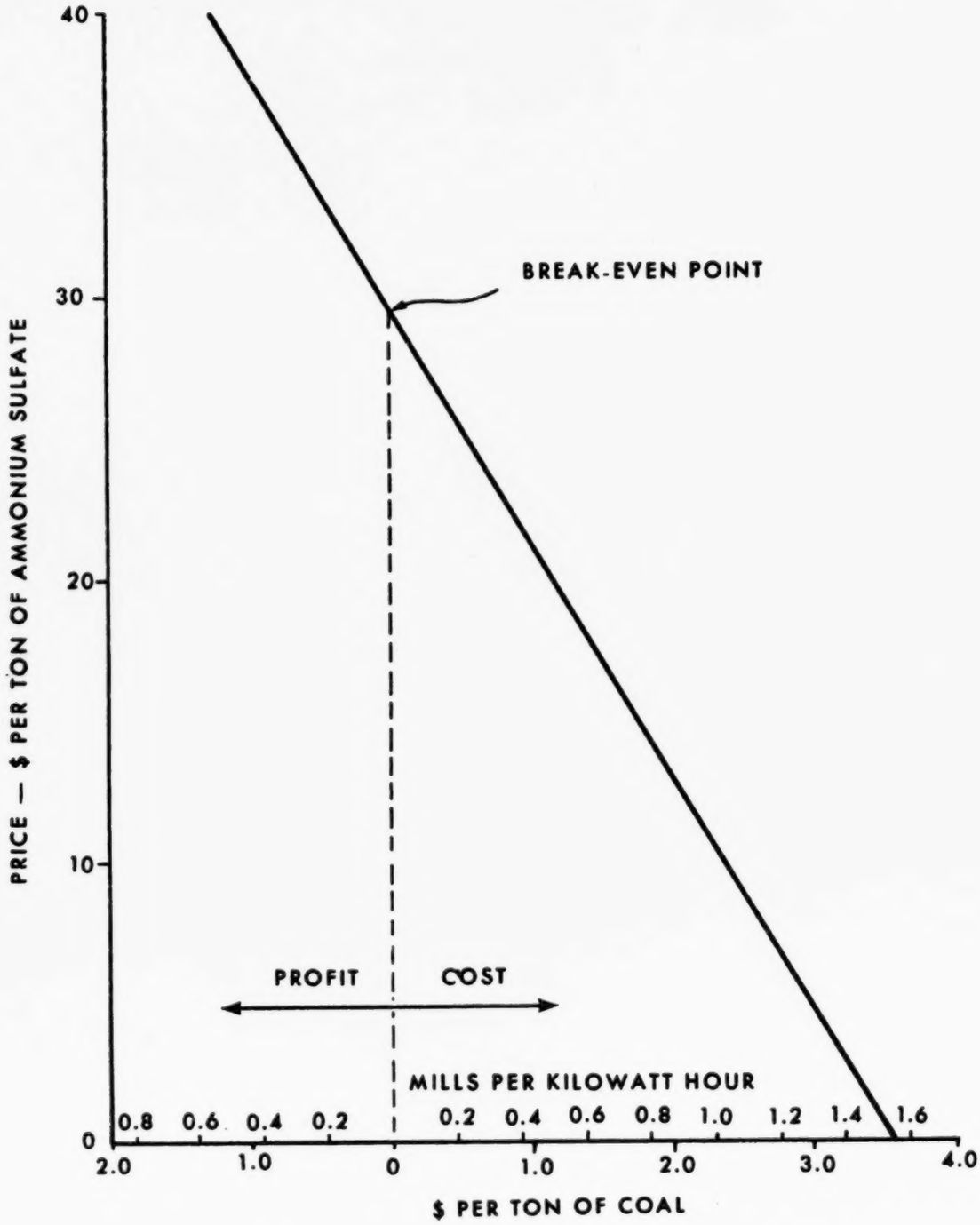


Figure 25. Effect of Product Credit on Operating Cost of Mitsubishi Process

Table 18

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @ 100 % Capacity

Category: Low Temperature Effluent

Name of Process T.V.A-Sulfuric Acid Process Flue Gas Rate 2.5 MMSCFM

MW 1,400

Fixed Capital Cost $56,000,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	594,000	2.76
2.	Direct Labor	105,000	0.48
3.	Supervision	31,200	0.14
4.	Maintenance, 5% of Fixed Capital	2,800,000	13.01
5.	Supplies, 15% of Maintenance	420,000	1.95
6.	Utilities	8,600,000	39.94
7.	Other		
8.	TOTAL DIRECT COST	12,550,200	58.28
9.	Payroll Burden, 20% of 2 & 3	27,300	0.12
10.	Plant Overhead, 50% of 2, 3, 4 and 5	1,678,100	7.80
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	1,705,400	7.92
15.	Depreciation, 10 % Fixed Capital/Yr.	5,600,000	26.00
16.	Taxes, 2% of Fixed Capital	1,120,000	5.20
17.	Insurance, 1% of Fixed Capital	560,000	2.60
18.	Other		
19.	TOTAL FIXED COST	7,280,000	33.80
20.	TOTAL OPERATING COST	21,535,600	100.00
21.	COST: $/Ton of Coal 4.69; Mill/kwh 1.94		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal ____; Mill/kwh ____		

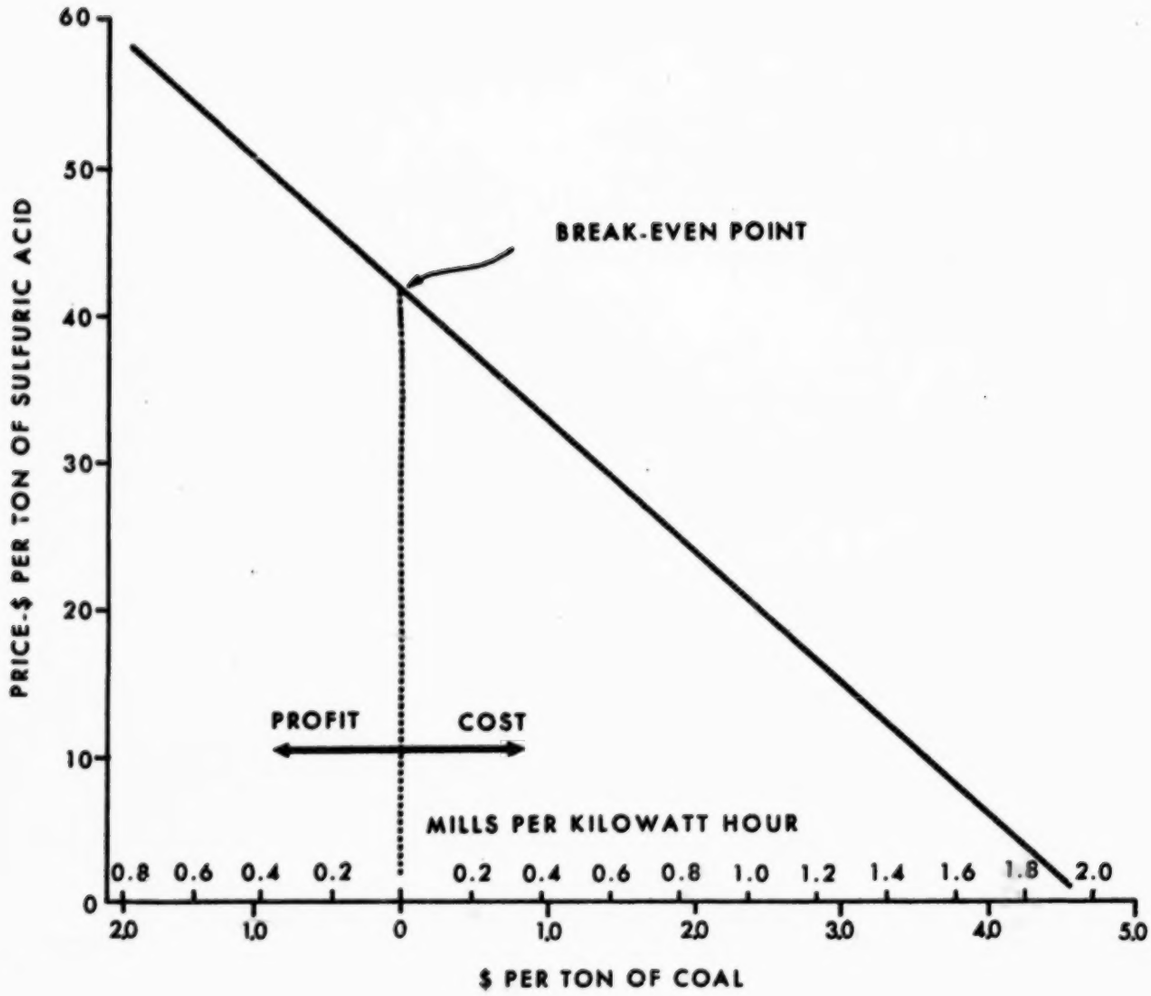


Figure 26. Effect of Product Credit on Operating Cost of T.V.A. -- Direct Acid Process

Table 19

OPERATING COST ESTIMATE SUMMARY

Basis: 330 Day/Year @ 10% Capacity

Category: Existing Power Plant (Low Temperature Effluent)

Name of Process Callery Chemical Company Process Flue Gas Rate 2.5 MMSCFM

MW 1400

Fixed Capital Cost 15,300,000

	ITEM	TOTAL $	PER CENT
1.	Raw Materials & Chemicals	1,015,000	21.49
2.	Direct Labor	105,000	2.22
3.	Supervision	31,200	0.67
4.	Maintenance, 5% of Fixed Capital	765,000	16,19
5.	Supplies, 15% of Maintenance	114,750	2.43
6.	Utilities	169,000	3.57
7.	Other		
8.	TOTAL DIRECT COST	2,199,950	46.57
9.	Payroll Burden, 20% of 2 & 3	27,200	0.57
10.	Plant Overhead, 50% of 2, 3, 4 and 5	508,000	10.75
11.	Pack & Ship		
12.	Waste Disposal		
13.	Other		
14.	TOTAL INDIRECT COST	535,200	11.32
15.	Depreciation, 10 % Fixed Capital/Yr.	1,530,000	32.39
16.	Taxes, 2% of Fixed Capital	306,000	6.48
17.	Insurance, 1% of Fixed Capital	153,000	3.24
18.	Other		
19.	TOTAL FIXED COST	1,989,000	42.11
20.	TOTAL OPERATING COST	4,724,150	
21.	COST: $/Ton of Coal 1.03 Mill/kwh 0.43		
22.	BY-PRODUCT CREDIT		
23.	ADJUSTED OPERATING COST		
24.	ADJUSTED COST: $/Ton of Coal Mill/kwh		

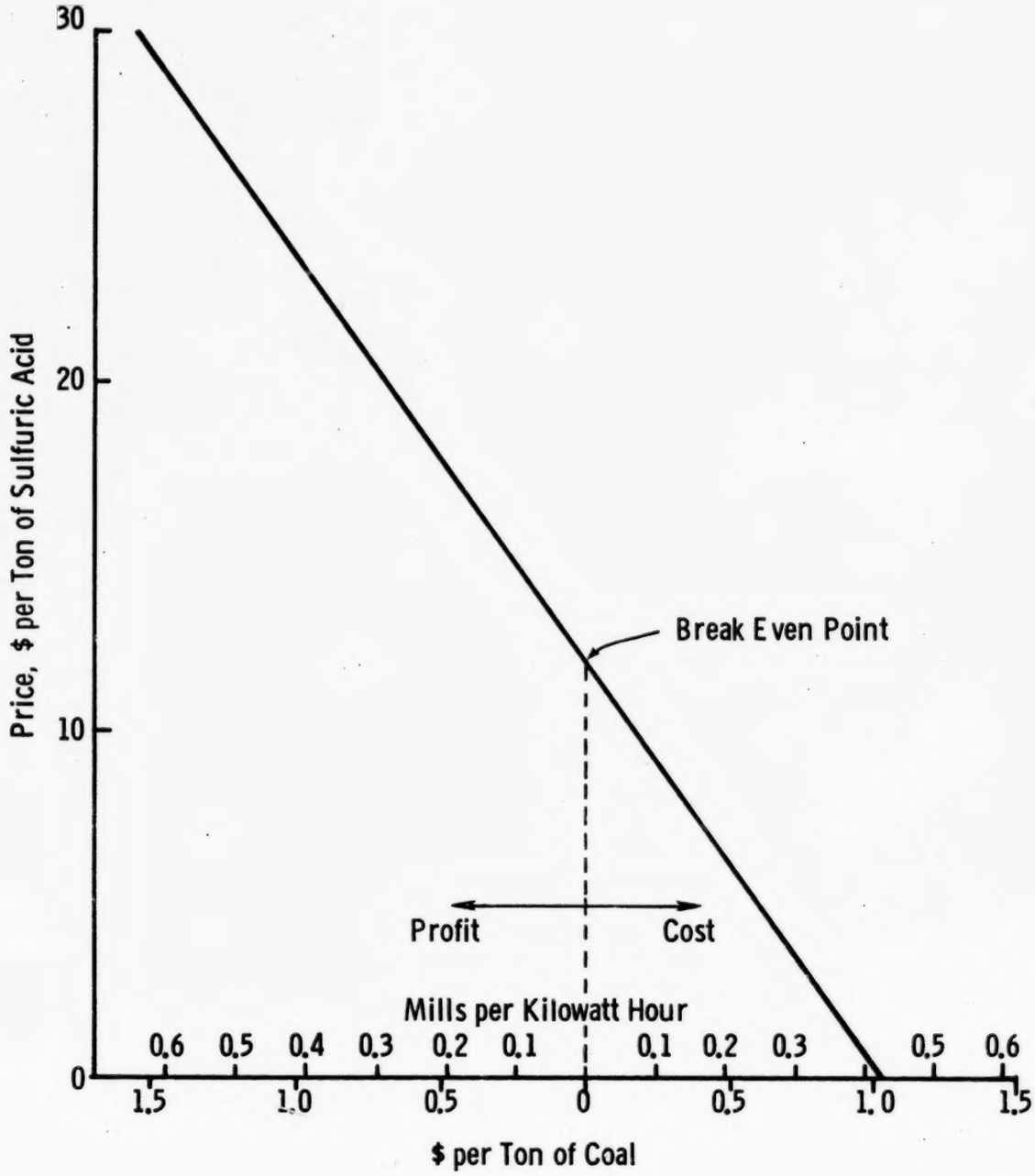


Figure 27. Effect of Product Credit on Operating Cost of Callery Process

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APPENDIX I

CONVERSION EFFICIENCY AND RATE EQUATION GRAPHS

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APPENDIX I

INDEX

Figure No.	Title	Page No.
1	Effect of Contact Time on Conversion at 500°C (calculated values for flue gas application)	118
2	Effect of Contact Time on Conversion at 450°C	119
3	Effect of Contact Time on Conversion at 425°C	120
4	Effect of Contact Time on Conversion at 425°C	121
5	Effect of Contact Time on Conversion by Mars & Maessen Equation at 400°C	122
6	Effect of Contact Time on Conversion at 400°C	123
7	Effect of Contact Time on Conversion at 375°C	124
8	Effect of W/F Ratio on Conversion at 500°C	125
9	Effect of W/R Ratio on Conversion at 450°C	126
10	Effect of W/F Ratio on Conversion at 425°C	127
11	Effect of W/F Ratio on Conversion at 425°C	128
12	Effect of W/F Ratio on Conversion by Mars & Maessen Equation at 752°F	129
13	Effect of W/F Ratio on Conversion at 400°C	130
14	Effect of W/F Ratio on Conversion at 375°C	131

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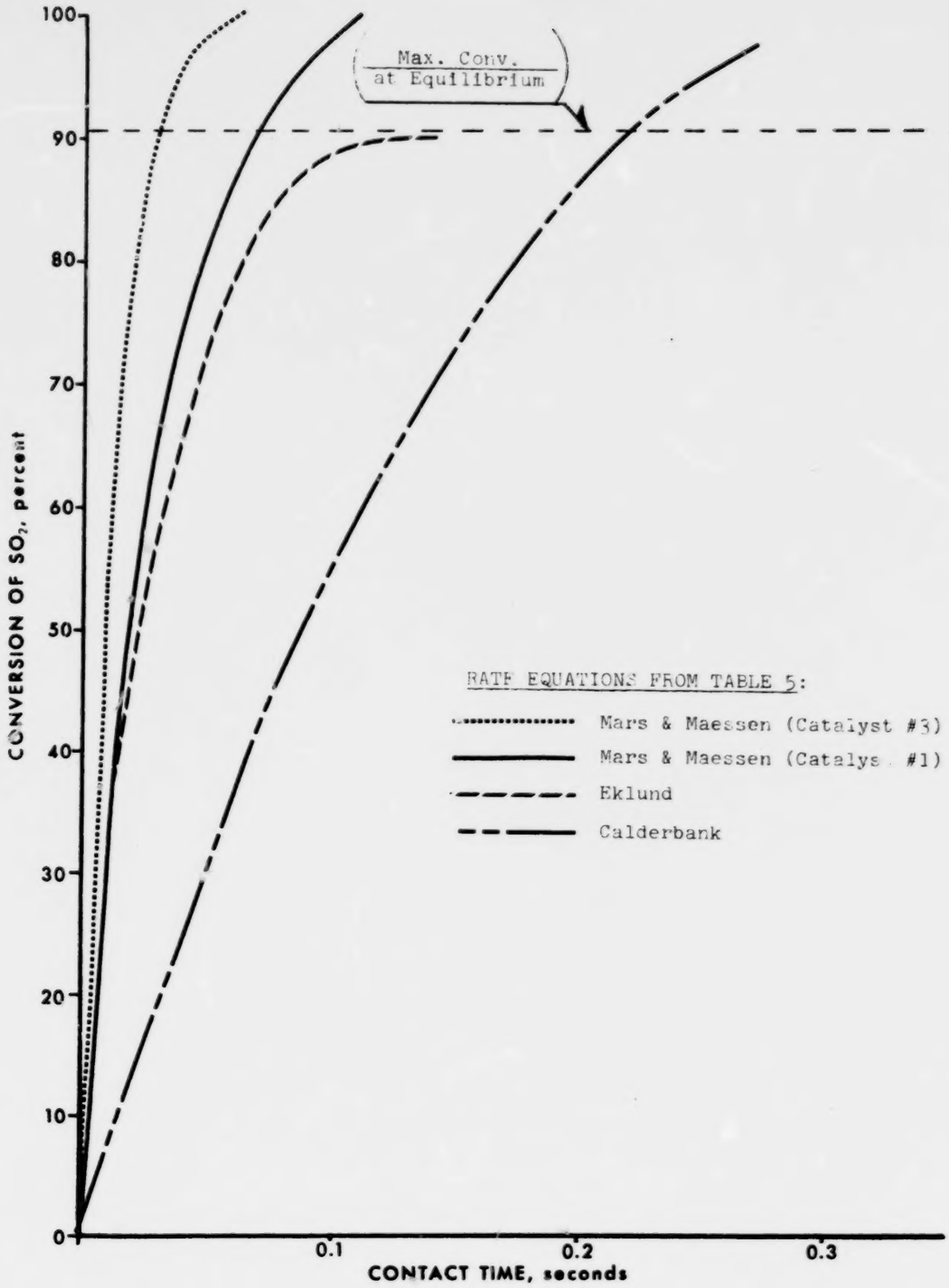

Figure 1. Effect of Contact Time on Conversion at 500°C (calculated values for flue gas application)

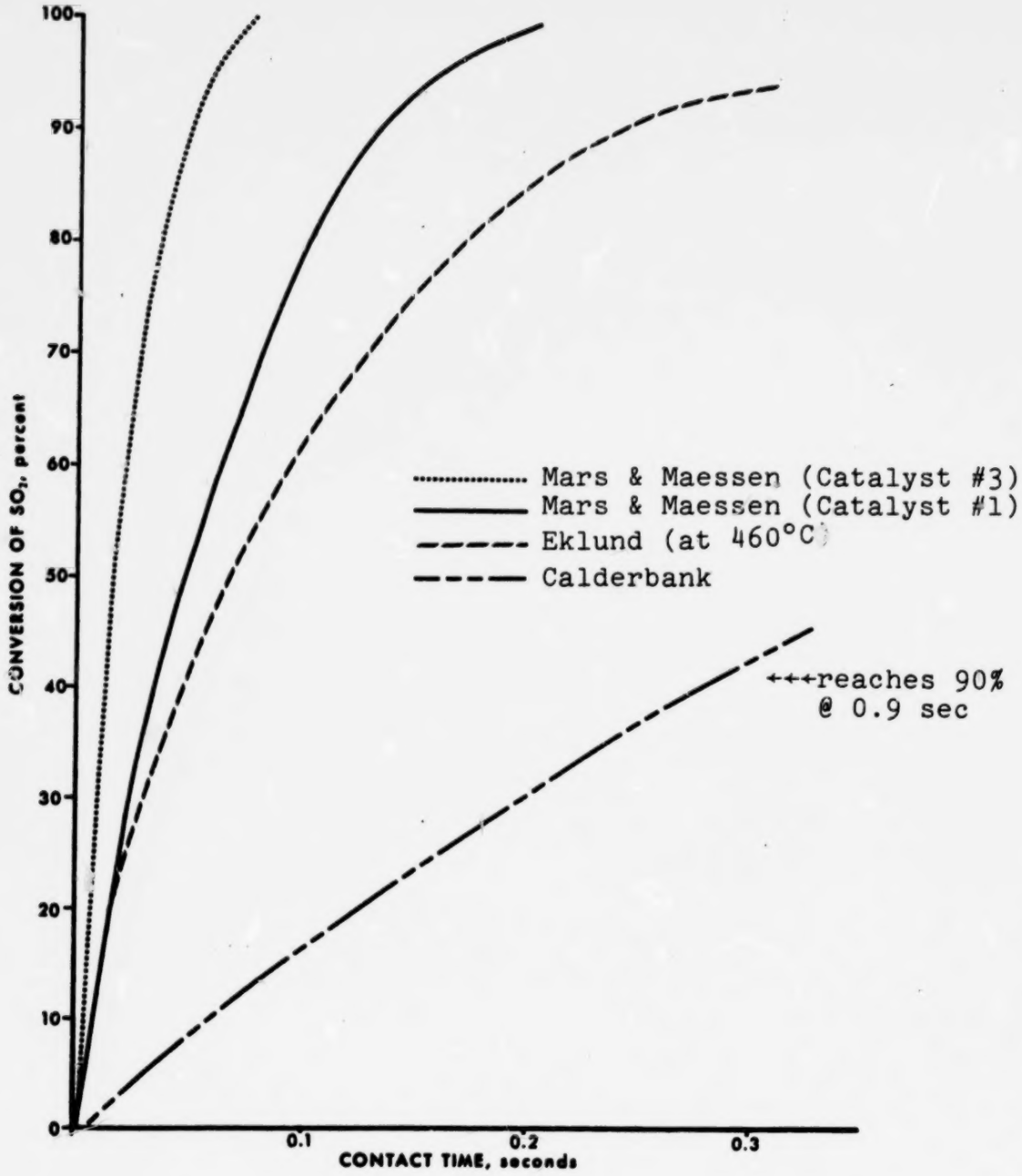

Figure 2. Effect of Contact Time on Conversion at 450°C

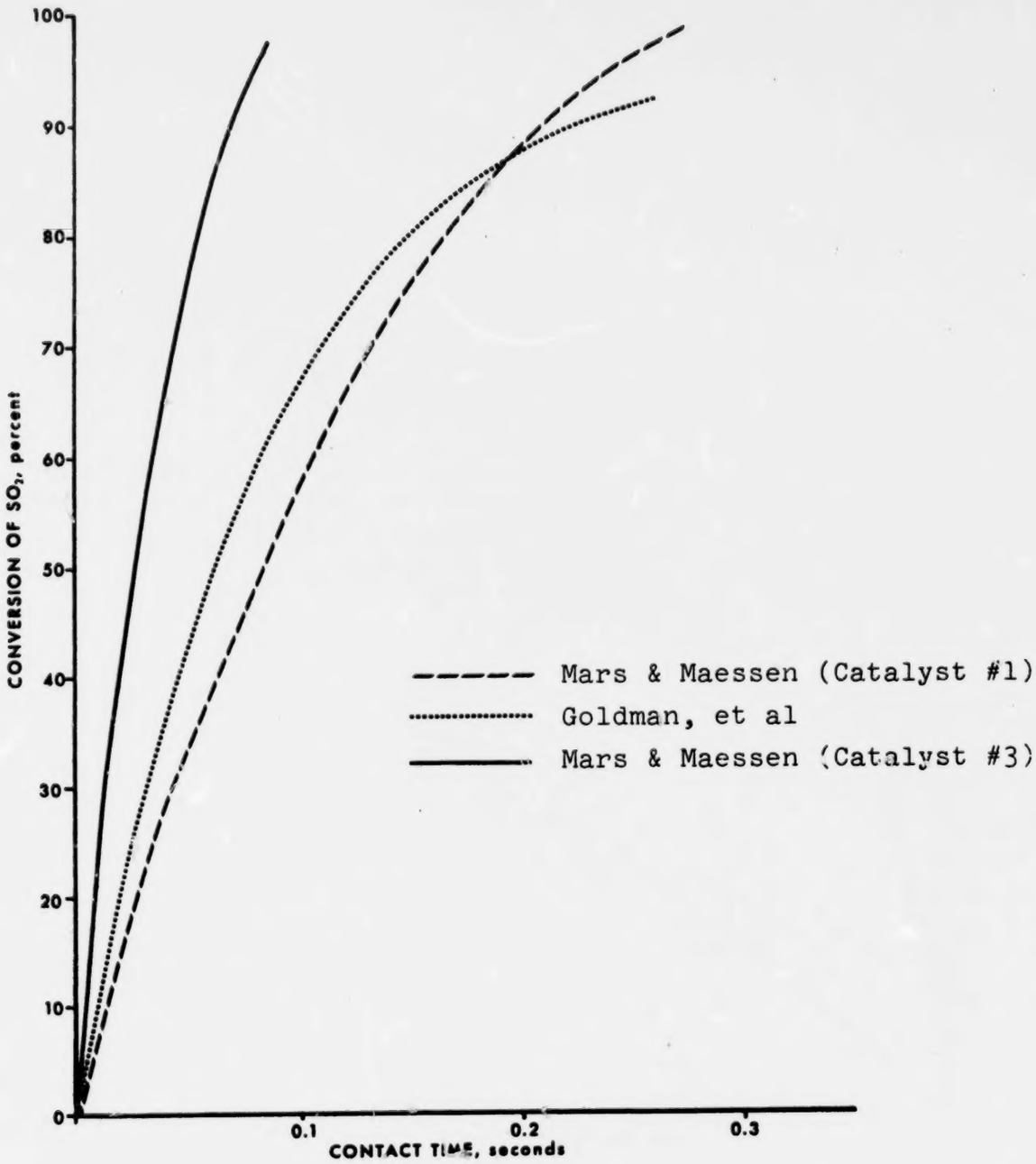

Figure 3. Effect of Contact Time on Conversion at 425°C

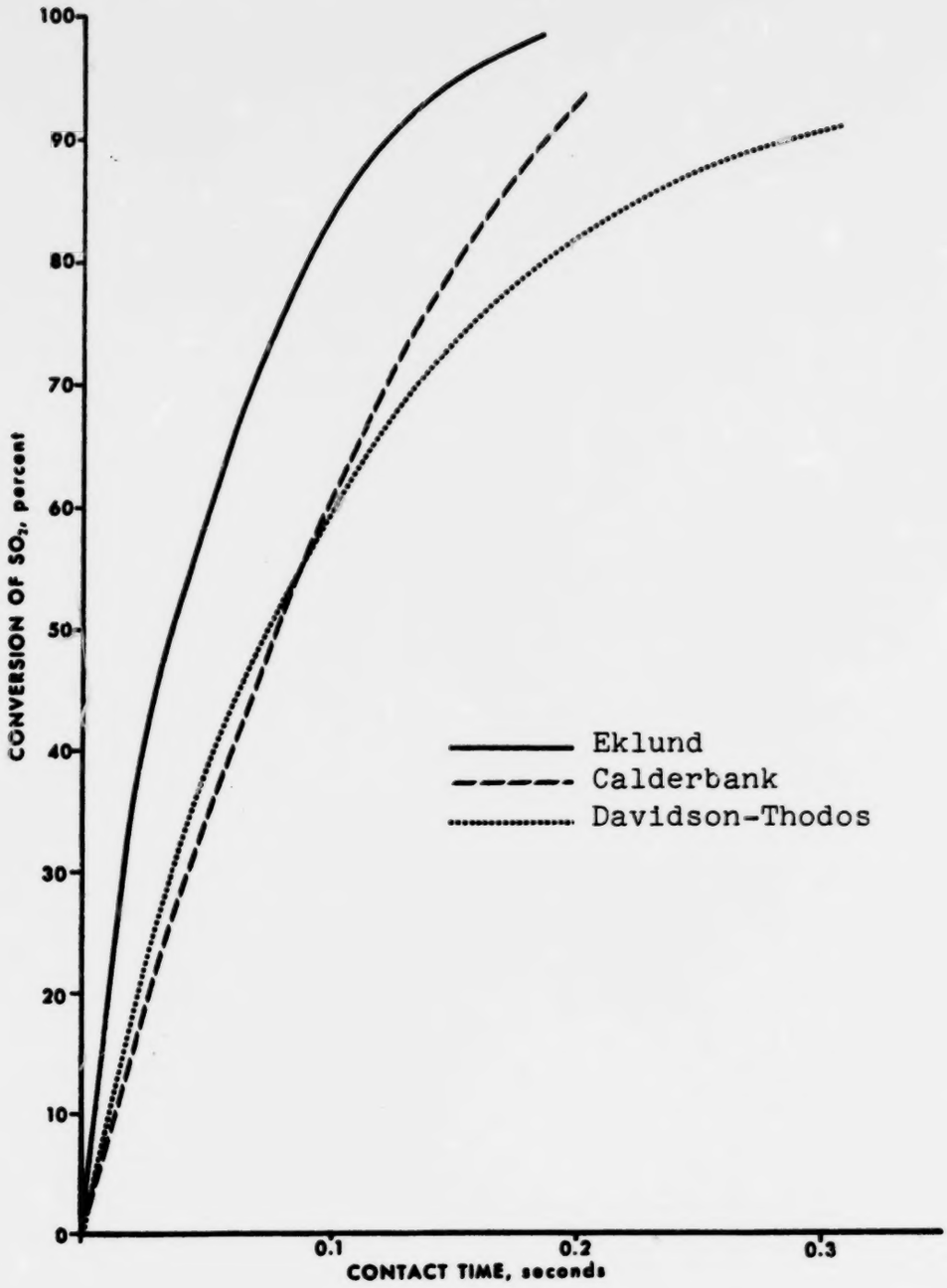

Figure 4. Effect of Contact Time on Conversion at 425°C

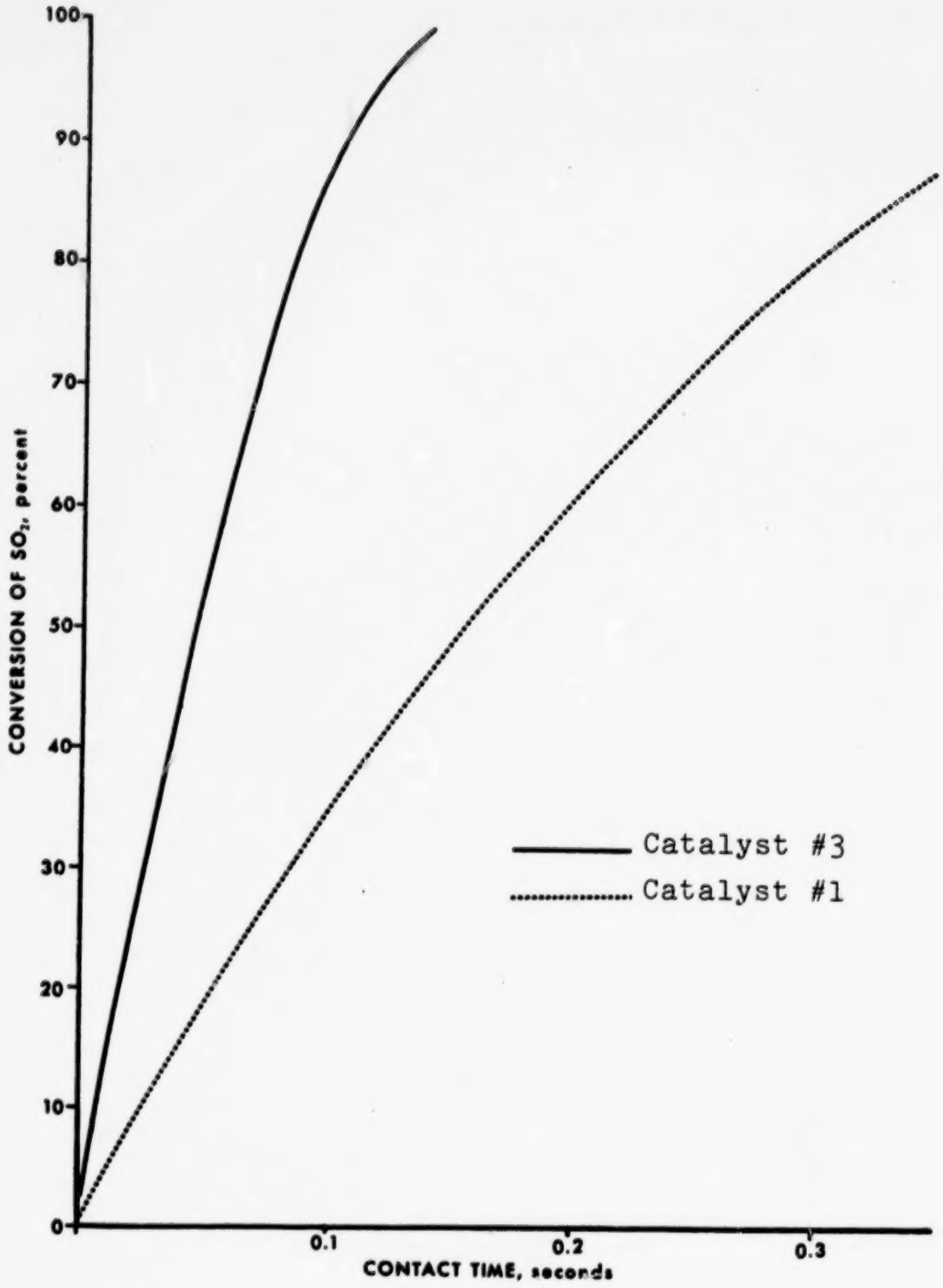

Figure 5. Effect of Contact Time on Conversion by Mars & Maessen Equation at 400°C

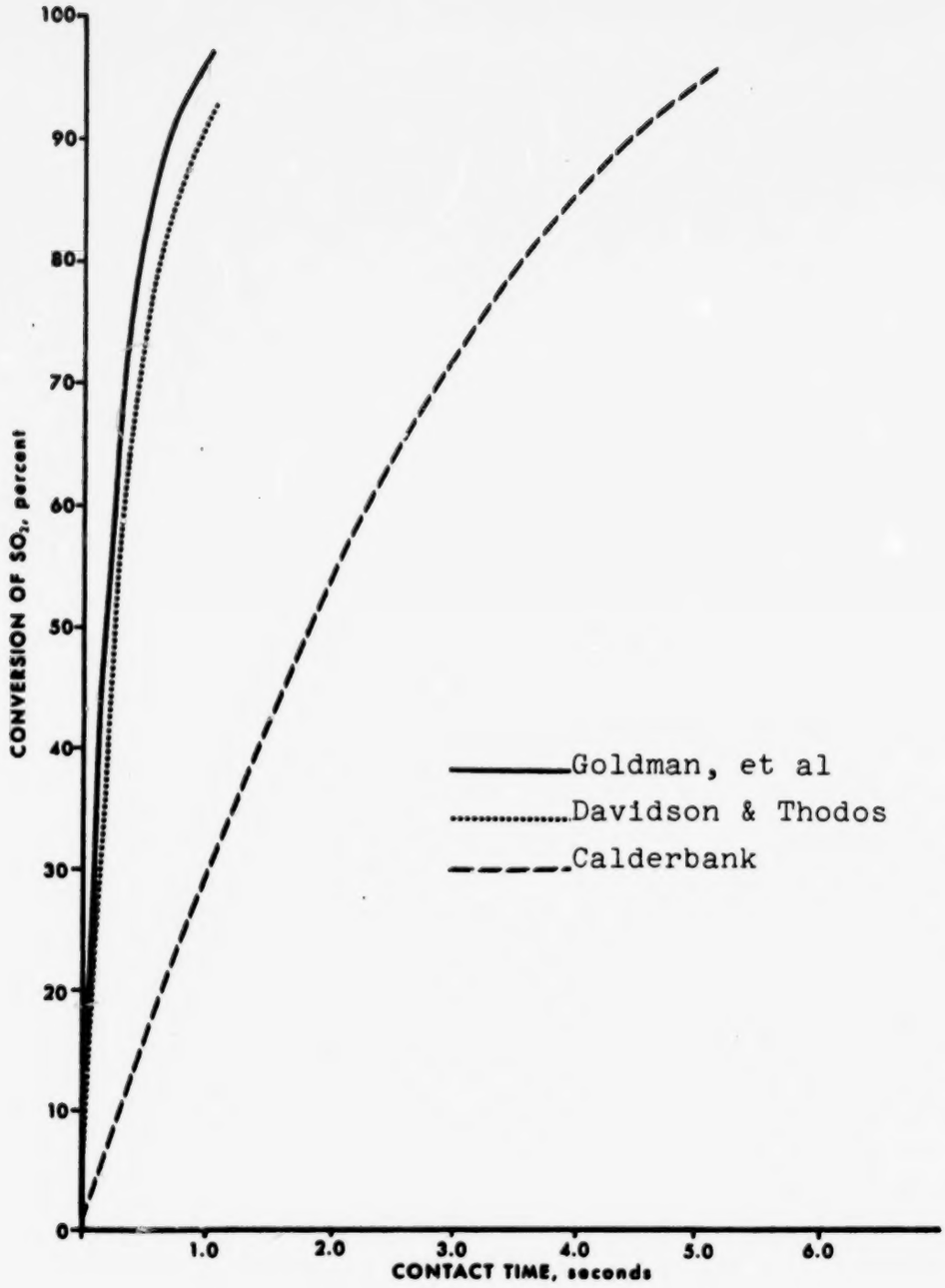

Figure 6. Effect of Contact Time on Conversion at 400°C

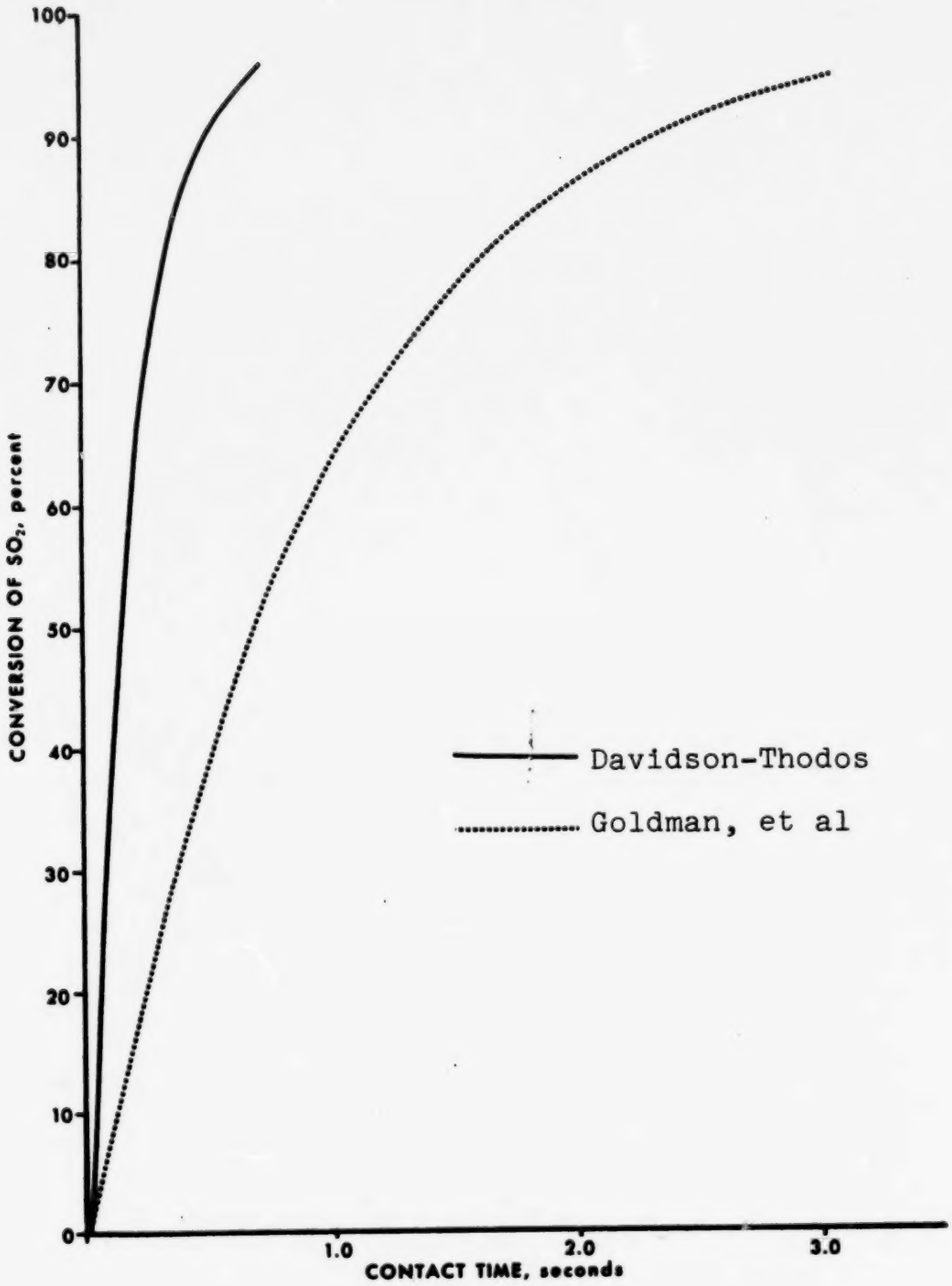

Figure 7. Effect of Contact Time on Conversion at 375°C

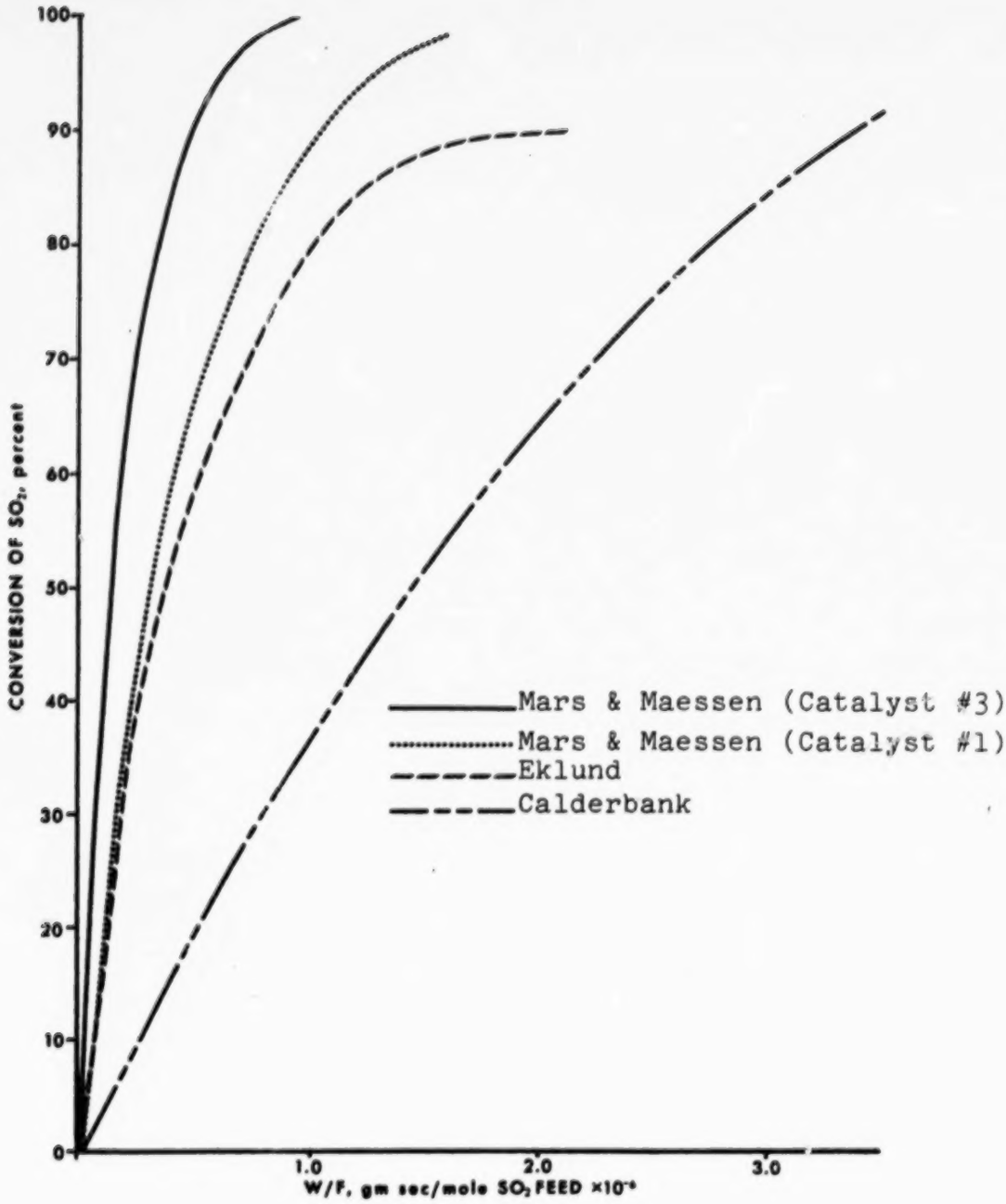

Figure 8. Effect of W/F Ratio on Conversion at 500°C

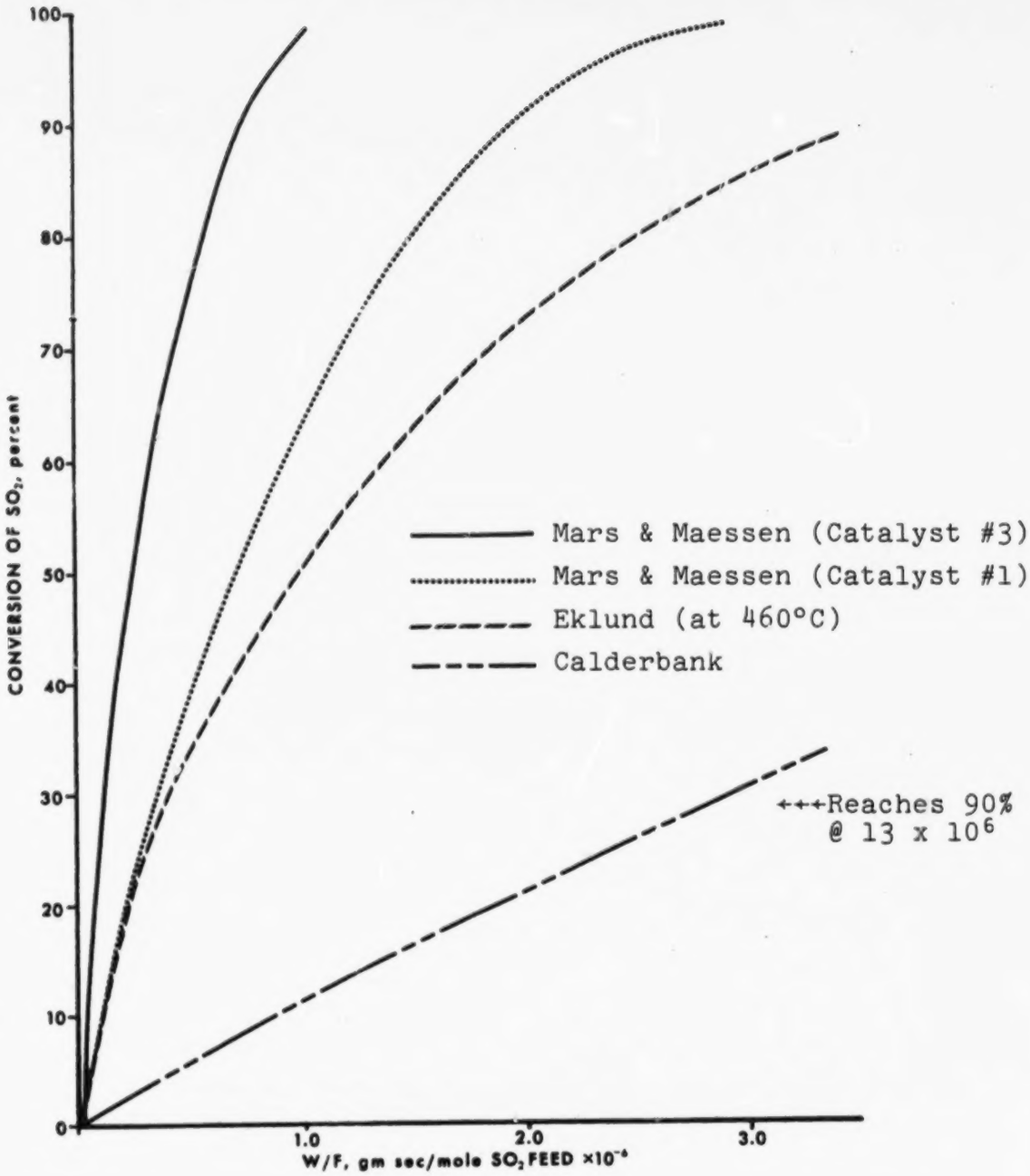

Figure 9. Effect of W/F Ratio on Conversion at 450°C

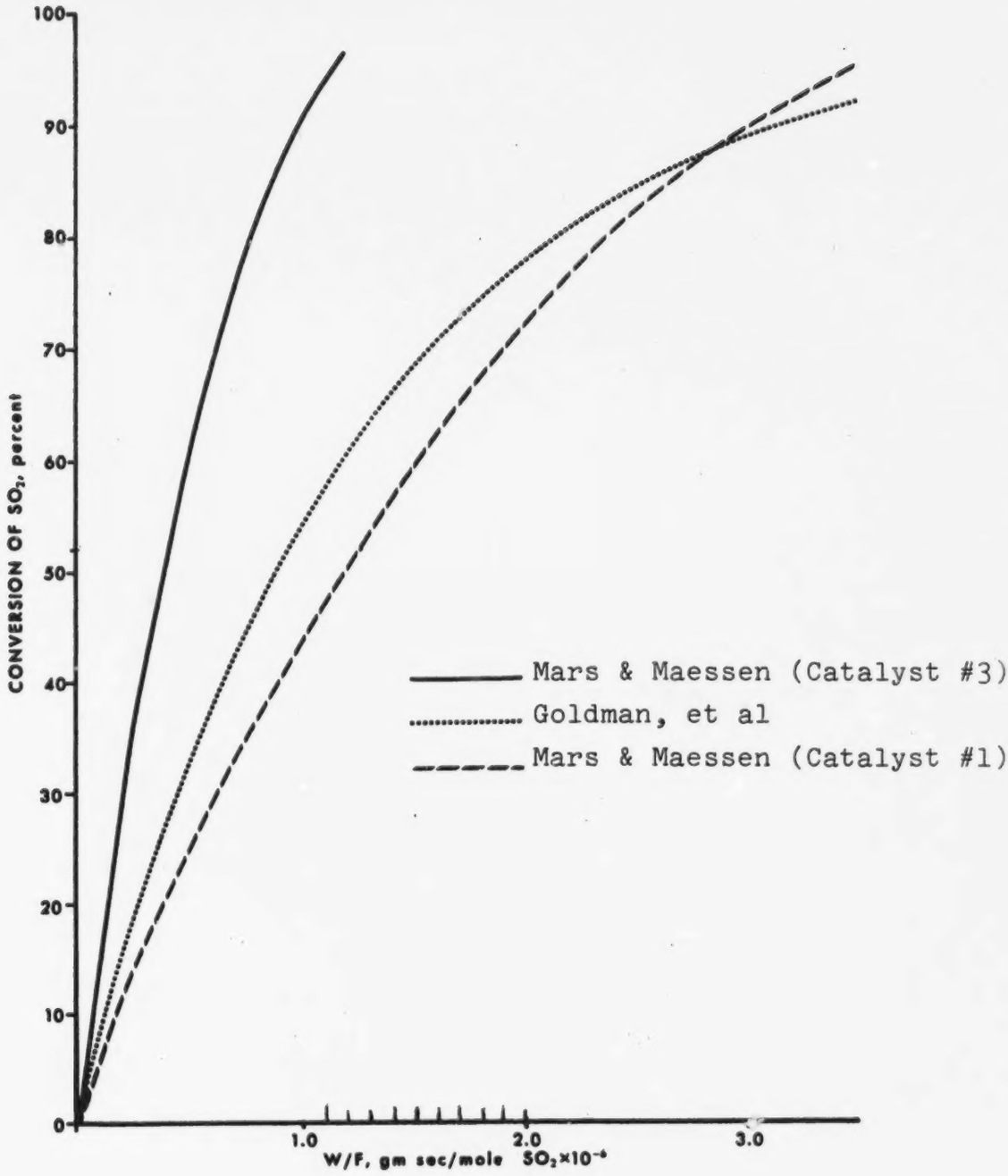

Figure 10. Effect of W/F Ratio on Conversion at 425°C

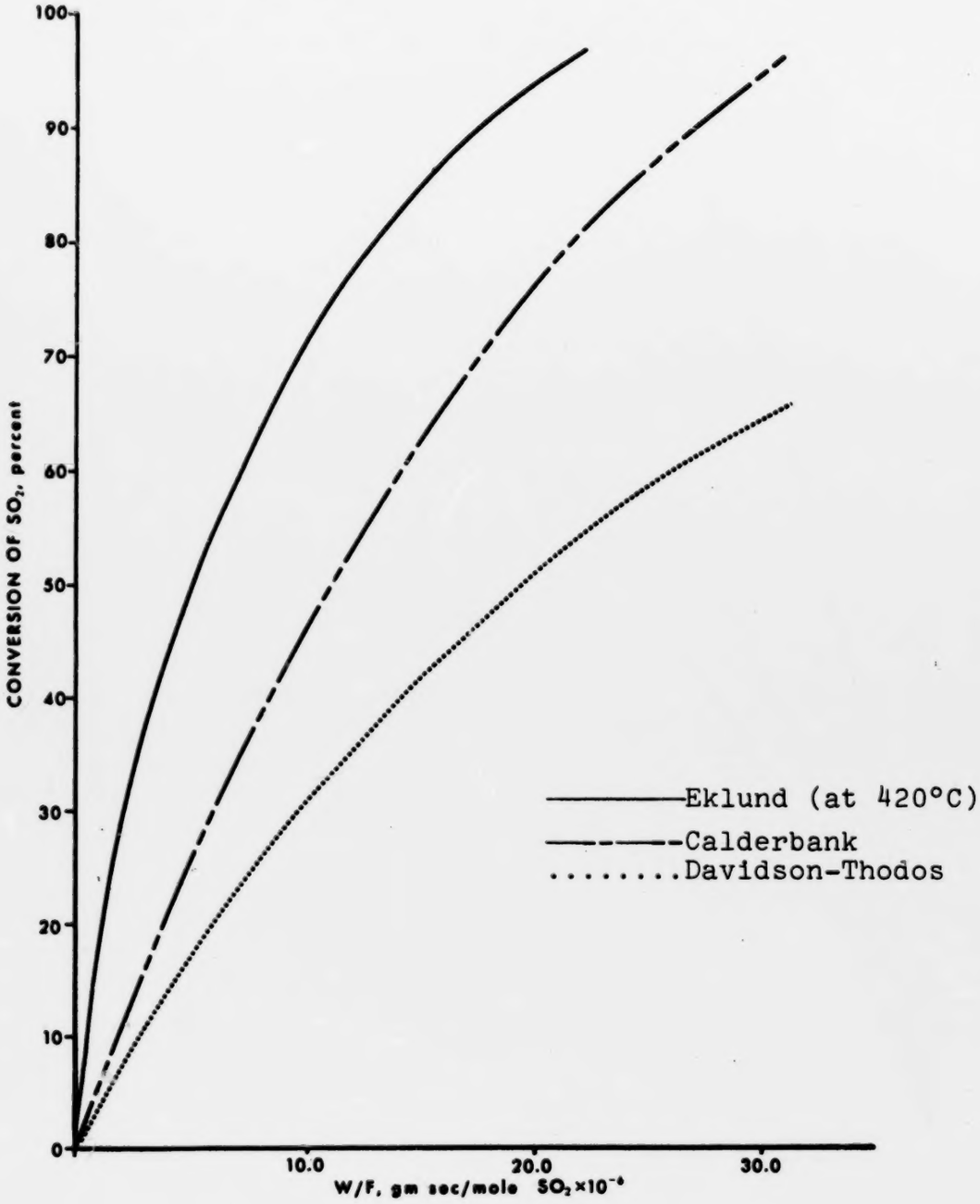

Figure 11. Effect of W/F Ratio on Conversion at 425°C

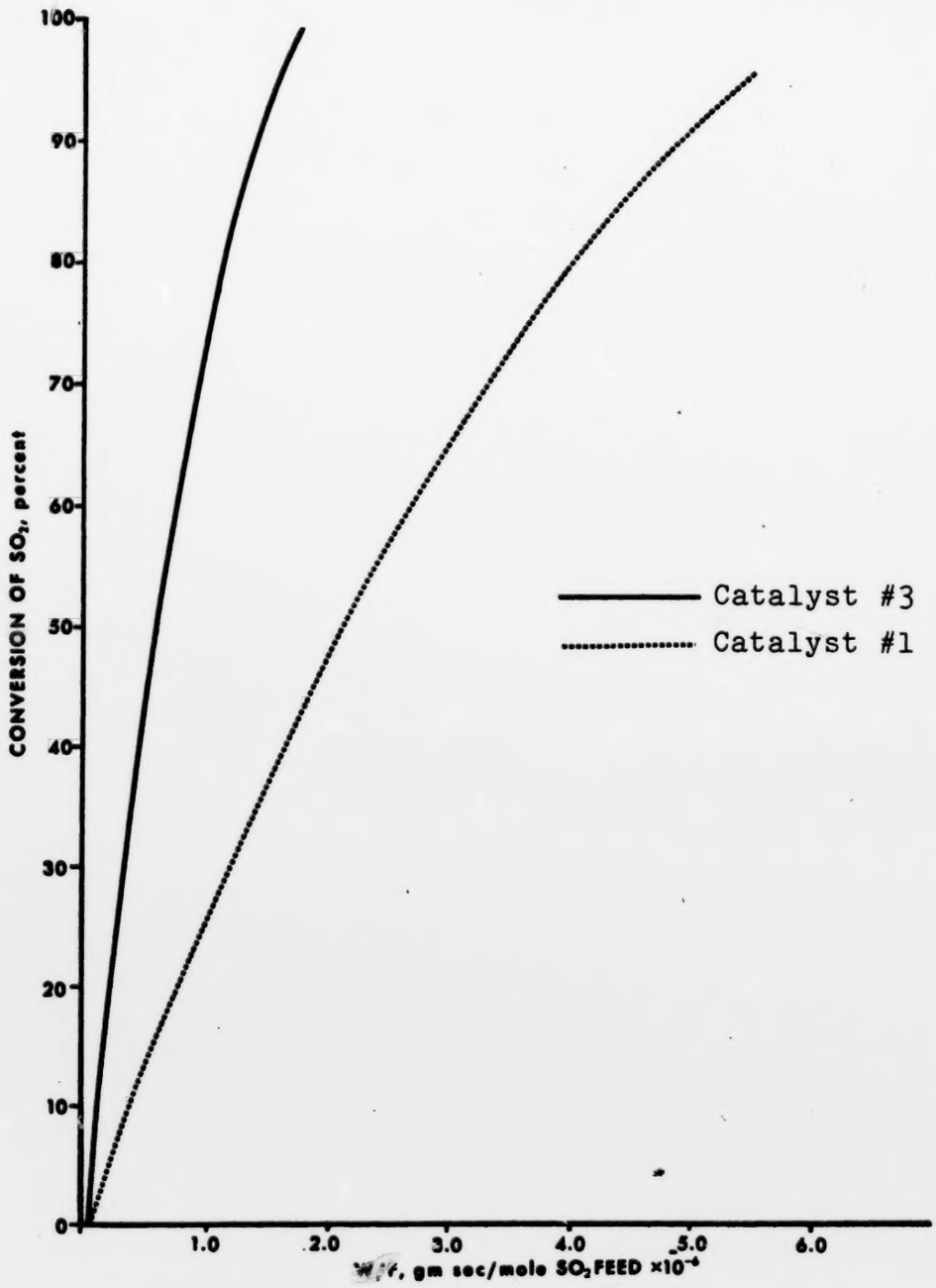

Figure 12. Effect of W/F Ratio on Conversion by Mars & Maessen Equation at 752°F

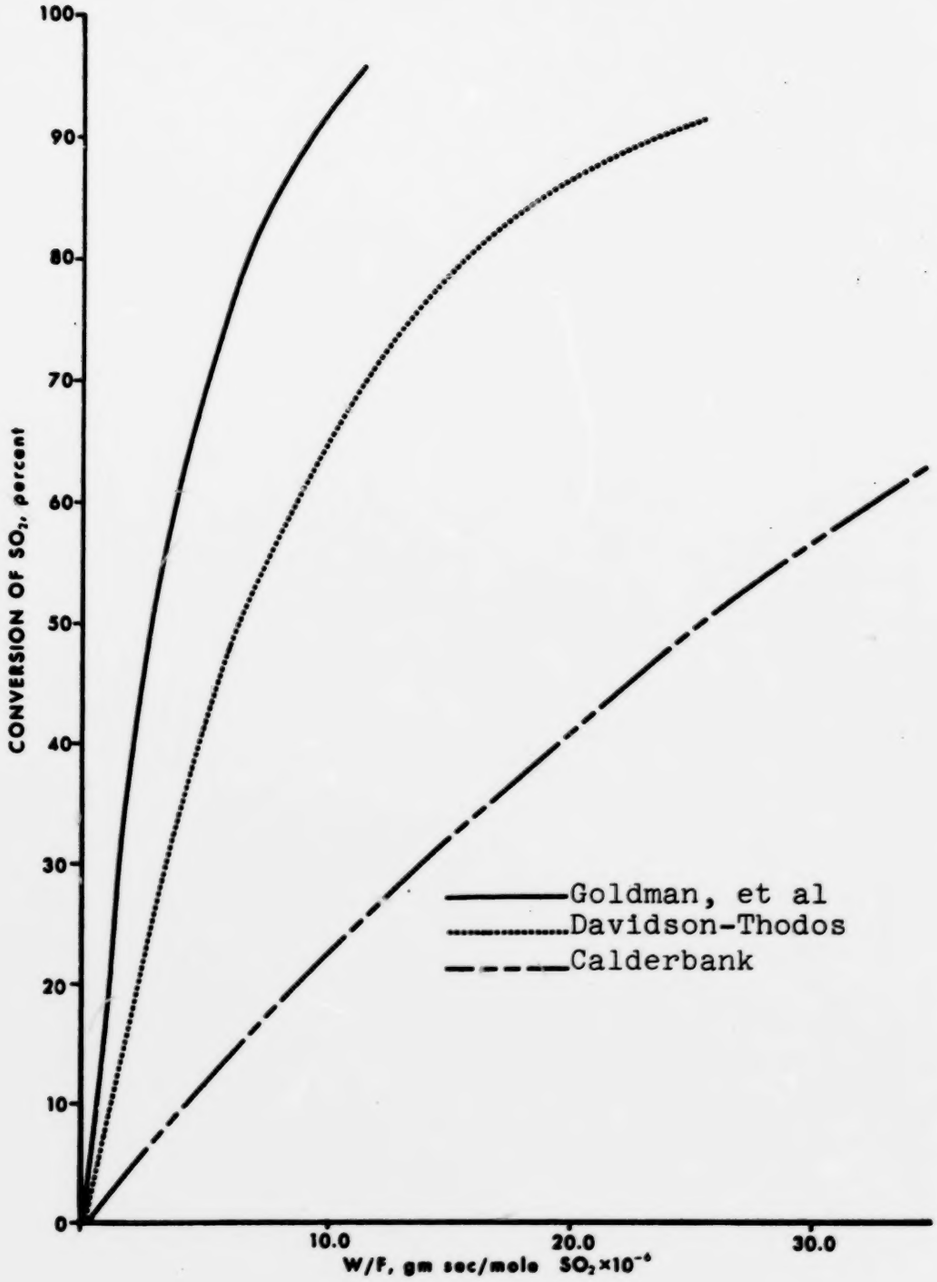

Figure 13. Effect of W/F on Conversion at 400°C

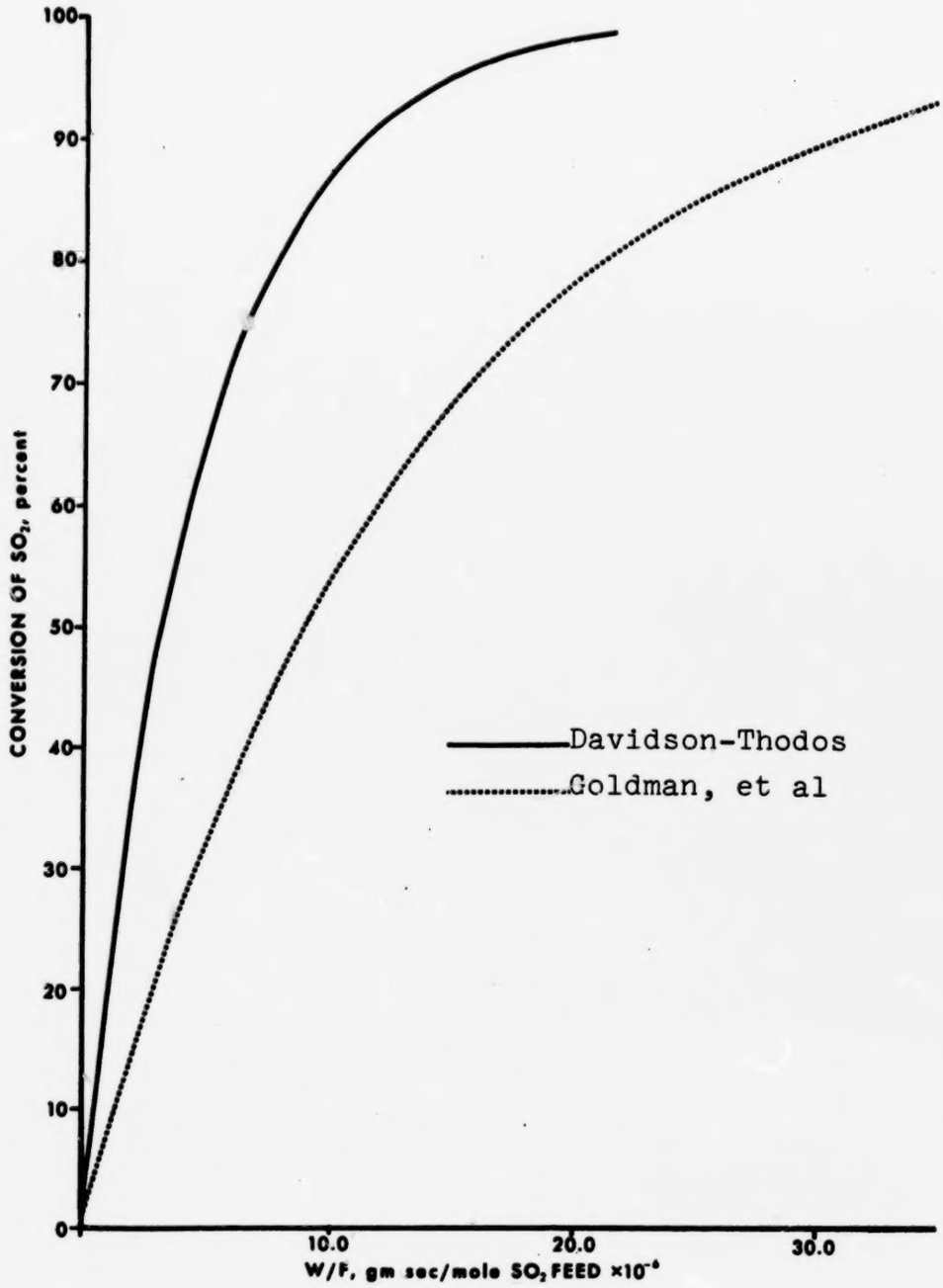

Figure 14. Effect of W/F Ratio on Conversion at 375°C

APPENDIX II

MATHEMATICAL MODELS AND COMPUTER PROGRAM LISTINGS

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APPENDIX II

INDEX

Title	Page No.
Reactant Partial Pressures and Conversion Fraction at Equilibrium for the Reaction $SO_2+1/2\ O_2 \rightleftarrows SO_3$ *	136
Partial Pressure and Conversion Fraction Computer Program Listing	139
Calculation of Percentage Conversion and Weight of Catalyst in an Isothermal Catalytic Reactor as a Function of Contact Time	141
Conversion Percentage and Catalyst Weight Calculation Computer Program Listing	149

* Calculated values

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REACTANT PARTIAL PRESSURES AND CONVERSION FRACTION AT EQUILIBRIUM FOR THE REACTION $SO_2 + 1/2\ O_2 \rightleftarrows SO_3$

Ref. 11 gives an approach for calculating reactant partial pressures and the equilibrium conversion fraction for the reaction $SO_2 + 1/2\ O_2 \rightarrow SO_3$. However, the equations for the reactant partial pressures,

$$PSO2 = \frac{2.00\ ay}{2.00 - a(1-y)} \qquad (1)$$

$$PSO3 = \frac{2.00\ a(1-y)}{2.00 - a(1-y)} \qquad (2)$$

$$PO2 = \frac{0.42 - 3a + ay}{2.00 - a(1-y)} \qquad (3)$$

[a is the initial partial pressure of SO_2 (atm.) in the burner gas obtained by the burning of sulfur in air, and y is the fraction of a remaining unconverted at equilibrium] were derived for the condition that sulfur is burned in air of 2 atm. pressure, and thus part of the oxygen is used to oxidize the sulfur to SO_2. In a catalytic reactor for oxidation of SO_2 in flue gases, different conditions prevail, the pressure is usually well below 2 atm. and the initial partial pressures of SO_2 and O_2 are lower than those for the case discussed above. The following will give the equations representative of the conditions prevailing in a catalytic reactor for the treatment of flue gases:

Let,

PTOT = Total pressure of all flue gas components in the catalytic reactor in atm.

a = <u>initial</u> vol. fraction of SO_2 in the flue gas

b = <u>initial</u> vol. fraction of O_2 in the flue gas

Assume that y is the fraction of a remaining unconverted at equilibrium. Then, at equilibrium

$$PO2 = \frac{\{b-0.5a(1-y)\}PTOT}{1-0.5a(1-y)} \qquad (4)$$

$$PSO2 = \frac{a \cdot y \cdot PTOT}{1-0.5a(1-y)} \qquad (5)$$

$$PSO3 = \frac{a(1-y)PTOT}{1-0.5a(1-y)} \qquad (6)$$

Also, for the reaction

$$SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$$

$$K_p = \frac{PSO3}{(PSO2)\cdot(PO2)^{1/2}} \qquad (7)$$

where K_p is the equilibrium constant.

Substitution of Eq's. (4), (5), (6) in Eq. (7) and rearranging yields

$$0.5a\{(PTOT)\cdot K_p^{\,2}-1\}y^3+\{(PTOT)\cdot K_p^{\,2}(b-0.5a)-(1-1.5a)\}y^2$$

$$+\{2-1.5a\}\cdot y+\{-1+0.5a\} = 0$$

The cubic equation (8) can be solved for y and for a range of values of a, b, PTOT and K_p. The only y values (roots) with physical meaning are those which are positive and ≤ 1. The calculated values of y can be substituted in Eq's. (1), (2), and (3) to determine the reactant partial pressures. The conversion fraction at equilibrium, i.e., the fraction of SO_2 converted into SO_3, is equal to $1-y$.

Temperature dependence of the partial pressures of the reactants can be evaluated by introducing K_p as a function of temperature into Eq. (8). Ref. 1 gives the following relationship between K_p and T (T = absolute temperature, °K).

$$\log K_p = \frac{4,956}{T} - 4.678 \qquad (9)$$

A computer program was developed for the solution of Eq's. (8) and (9) and for the computation of the partial pressures and the conversion fraction. This program allows for a parametric evaluation of the reaction $SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$ for a range of total pressures, initial vol % of SO_2 and O_2, and temperatures.

The next two pages show a FORTRAN-IV listing and a sample print-out, respectively.

Table 1

FORTRAN-IV PROGRAM FOR CALCULATING EQUILIBRIUM CONVERSION VALUES

```
// FOR
*IOCS(CARD,1132 PRINTER)
*EXTENDED PRECISION
* LIST ALL
      REAL KP,KP2,INT
      DIMENSION B(5),AA(6)
      READ(2,5)L,(AA(I),I=1,L)
      READ(2,5)K,(B(I),I=1,K)
    5 FORMAT(I5,6F5.0)
      DO 60 J=1,L
      DO 60 I=1,K
      WRITE(3,109)
  109 FORMAT('1')
      PTOT=1.1
      A=AA(J)
      B(I)=B(I)*100.
      A=A*100.
      WRITE(3,108)PTOT,A,B(I)
  108 FORMAT(10X,'TOTAL PRESSURE (ATM)',F8.2,//,
     1        10X,'INITIAL VOLUME PERCENT OF SO2=',F8.2//,
     2        10X,'INITIAL VOLUME PERCENT OF O2=',F8.2//)
      A=A/100.
      B(I)=B(I)/100.
      WRITE(3,100)
  100 FORMAT(5X,'TEMP',16X,'PSO2',18X,'PO2',15X,'PSO3',15X,'KSUBP',16X,
     1     'EQU. CON.',//)
      T=450.0
      N=0
   10 N=N+1
      T=T+50.0
      KP=10.0**(4956.0/T-4.678)
      KP2=KP**2
      D=0.5*A*(PTOT*(KP2-1.0))
      AB=B(I)
      P=(PTOT*KP2*(AB-0.5*A)-(1.0-1.5*A))
      P=P/D
      Q=2.0-1.5*A
      Q=Q/D
      R=-1.0+0.5*A
      R=R/D
      TEST=D+P+Q+R
      IF(TEST)15,16,16
   15 Y=1.0
      GO TO 50
   16 INT=0.1
      Y=1.1
   30 SY=Y
      Y=Y-INT
      SZ=Z
      Z=D*Y**3+P*Y**2+Q*Y+R
      IF(Z)20,20,30
   20 Y=SY
      Z=SZ
      INT=INT/10
      IF(INT-1.0E-10)50,50,30
   50 CONTINUE
      PSO2=2.0*A*Y/(2.0-A*(1.0-Y))
      PSO3=2.0*A*(1.0-Y)/(2.0-A*(1.0-Y))
      PO2=(0.42-3.0*A+A*Y)/(2.0-A*(1.0-Y))
      EC=(1.0-Y)*100.
      WRITE(3,103)T,PSO2,PO2,PSO3,KP,EC
  103 FORMAT(2X,E12.5,5(8X,E12.5),I4)
      IF(T-1200.0)10,60,60
   60 CONTINUE
      CALL EXIT
      END
```

Table 2

SAMPLE PRINT-OUT FROM COMPUTER PROGRAM FOR CALCULATING EQUILIBRIUM CONVERSION VALUES

TOTAL PRESSURE (ATM) 1.10

INITIAL VOLUME PERCENT OF SO2= 0.30

INITIAL VOLUME PERCENT OF O2= 2.50

TEMP	PSO2	PO2	PSO3	KSUBP	EQU. CON.
0.50000E 03	0.22271E-07	0.20580E 00	0.30044E-02	0.17139E 06	0.99999E 02
0.55000E 03	0.33979E-06	0.20580E 00	0.30041E-02	0.21523E 05	0.99988E 02
0.60000E 03	0.30520E-05	0.20580E 00	0.30014E-02	0.38194E 04	0.99898E 02
0.65000E 03	0.17291E-04	0.20581E 00	0.29871E-02	0.88433E 03	0.99424E 02
0.70000E 03	0.67437E-04	0.20583E 00	0.29369E-02	0.25234E 03	0.97755E 02
0.75000E 03	0.19978E-03	0.20588E 00	0.28044E-02	0.85113E 02	0.93349E 02
0.80000E 03	0.47394E-03	0.20599E 00	0.25298E-02	0.32885E 02	0.84221E 02
0.85000E 03	0.91191E-03	0.20617E 00	0.20912E-02	0.14209E 02	0.69634E 02
0.90000E 03	0.14395E-02	0.20638E 00	0.15627E-02	0.67401E 01	0.52052E 02
0.95000E 03	0.19275E-02	0.20657E 00	0.10740E-02	0.34581E 01	0.35782E 02
0.10000E 04	0.22963E-02	0.20672E 00	0.70474E-03	0.18967E 01	0.23483E 02
0.10500E 04	0.25414E-02	0.20681E 00	0.45919E-03	0.11015E 01	0.15302E 02
0.11000E 04	0.30000E-02	0.20700E 00	0.00000E 00	0.67213E 00	0.00000E 00
0.11500E 04	0.30000E-02	0.20700E 00	0.00000E 00	0.42811E 00	0.00000E 00
0.12000E 04	0.30000E-02	0.20700E 00	0.00000E 00	0.28313E 00	0.00000E 00

Calculation of Percentage Conversion and Weight of Catalyst in an Isothermal Catalytic Reactor as a Function of Contact Time

The calculations described below will depend on the availability of a kinetic equation for the reaction expressing the rate of conversion, in this case of SO_2, as a function of the various relevant variables.

$$v = f(P_{SO_2}, P_{O_2}, P_{SO_3}, T, K_1 \cdot\cdot K_n) \qquad (1)$$

where: v is the velocity of the conversion per gram of catalyst (moles SO_2/sec-g.)

T is the temperature (°K)

$K_1 \cdot\cdot K_n$ are various parameters of the kinetic equation such as equilibrium constants which may or may not also be functions of T.

P_x is the partial pressure of component x (atm.)

Using this expression it is possible to calculate the rate of the conversion for a given set of reaction conditions. What we would then like to do is to be able to use the velocities calculated to compute the composition of the gas stream passing through the catalyst as a function of time.

If we assume that we start out with a feed stream of initial composition P_{O_2}, P_{SO_2}, and P_{SO_3} at temperature T, we can use equation (1) to calculate v_o the instantaneous rate of reaction under the initial conditions.

Using Equation (2) we can calculate the change in the number of moles of SO_3 produced (Δm_{SO_3}) in a time Δt. Since

$$\Delta m_{SO_3} = v_o \Delta t \qquad (2)$$

the change in the pressure of SO_3 (ΔP_{SO_3}) is directly proportional to Δm_{SO_3} (Eq. 3) it should be possible to calculate the former quantity.

$$P_{SO_3} = K_C \Delta m_{SO_3} \qquad (3)$$

Then using the expressions:

$$P_{O_2} = P_{O_2} - 1/2 \Delta P_{SO_3} \qquad (4)$$

$$P_{SO_2} = P_{SO_2} - \Delta P_{SO_3} \qquad (5)$$

$$P_{SO_3} = P_{SO_3} + \Delta P_{SO_3} \qquad (6)$$

the concentration of the feed gas at the end of this time increment Δt can be calculated. This process can be repeated for the next time increment Δt using the new pressures calculated in place of the initial pressures, to calculate the composition of the gas stream at the end of the time period $2\Delta t$.

Repetition of this process will allow one to calculate the composition of the gas stream at any given contact time. This information can be substituted into Equations (7) and (8) to calculate fraction of SO_2 converted (α) and percent conversion ($\%\alpha$) of SO_2 for that time period.

$$\alpha = \frac{P_{SO_3}}{P_{SO_2}} \tag{7}$$

$$\%\alpha = \frac{P_{SO_3}}{P_{SO_2}} \times 100 \tag{8}$$

All that remains in the way of making these calculations is being able to find a value for K_c, the proportionality factor between ΔP_{SO_3} and Δm_{SO_3}. This K_c can be derived as follows:

Let F be the volume flow rate of gas stream in the reactor at temperature T. If T is constant then the volume flow rate, F, is a constant throughout the reactor. Therefore, the incremental time, Δt, it takes for a unit volume of gas to flow through an incremental volume, Δv_c, of catalyst bed is given by:

$$\Delta t = \frac{\Delta v_c}{F} \tag{9}$$

For a catalyst of bulk density, ρ, Δv_c can be related to the incremental weight of the catalyst ΔW as follows:

$$\Delta v_c = \Delta W/\rho \tag{10}$$

Substituting Δv_c in Equation (9) yields

$$\Delta t = \frac{\Delta W}{\rho F} \tag{11}$$

or

$$W = \rho F \Delta t \tag{12}$$

Using the ideal gas law, the number of moles of SO_3 passing through the catalyst bed at any contact time t per gram of catalyst is given by:

$$m_{SO_3} = \frac{P_{SO_3}F}{RTW} \tag{13}$$

Therefore, during a time increment Δt

$$\Delta m_{SO_3} = \frac{\Delta P_{SO_3}F}{RTW} \quad \Delta t \tag{14}$$

If we substitute Equation (12) into Equation (14) we obtain

$$\Delta m_{SO_3} = \frac{\Delta P_{SO_3}F}{\rho F \Delta t RT} \quad \Delta t \tag{15}$$

or

$$\Delta P_{SO_3} = \rho RT \Delta m_{SO_3} \tag{16}$$

If we compare Equation (16) with Equation (3) we find that

$$K_c = \rho RT \tag{17}$$

A further quantity that would be helpful to calculate is the total amount of catalyst necessary to effect a particular percent conversion of SO_2. This quantity can be calculated in the following manner. If we assume that as the gas passes through an increment of catalyst weighing dW the change in fraction converted is $d\alpha$. Then:

$$dW = \frac{F}{v} \, d\alpha \tag{18}$$

where v reaction rate is a function of α (conversion)

Since we do not have the explicit form of the expression for the instantaneous velocity v as a function of α at constant temperature, we cannot integrate Equation (18) analytically. We can, however, integrate this equation numerically using the difference formula:

$$W^k = W^{k-1} + \frac{F}{V^k} \Delta\alpha^k$$

where W^k is the weight of catalyst which has contacted the gas stream after the kth increment of contact time.

V^k = The velocity of reaction at the start of the kth increment of contact time.

$\Delta\alpha^k$ = The change in fraction SO_2 converted during the kth increment of contact time.

We have written two programs for an IBM 1130 computer which makes the calculations described above. The mainline program CONV. handles all the input and output. In addition, it calculates the pressures of reactants and products in the gas stream, conversions and the W/F ratio as a function of contact time. This program is listed on pages 149 through 152.

CONV. contains a call to the subroutine REACV. which calculates the velocity of the conversion in moles of SO_3 per second per gram of catalyst as a function of partial pressures of the components and the absolute temperature.

An illustration of one form of the subroutine REACV which calculates the velocity of reaction according to the equations of Davidson and Thodos is listed on page 76.

It is assumed in all these calculations that the conversion reaction takes place isothermally. We have also assumed that the bulk density of the catalyst bed is 0.75 g/cc.

The input and outputs from these programs are arranged as follows:

I N P U T

Card 1

Case title — Columns 1-80

Card 2

TII	=	integration interval (sec.)	unformatted*
TP	=	printing interval (sec.)	
TFV	=	upper limit of integration (sec.); lower limit is zero	
NC	=	number of equation constants to be read in on Card 4	

Card 3

PO	=	initial pressure of O_2 in gas stream (atm.)	unformatted
P2	=	initial pressure of SO_2 in gas stream (atm.)	
P3	=	initial pressure of SO_3 in gas stream (atm.)	

*unformatted input must be separated on data cards at least one blank. The subroutine READP which allows unformatted input can be furnished on request.

Card 4

C(1) = temperature (°C)

C(2) ⎫
⋮ ⎬ equation constants
C(NC) ⎭

} unformatted

a typical input listing is given on page 76.

O U T P U T

The following information is printed by the computer as output.

1) case title
2) integration interval (sec.)
3) print interval (sec.)
4) K(EQ) the equilibrium constant for the O_2-SO_2-SO_3 equilibrium
5) temperature in degrees centigrade
6) PO_2(F) the initial feed composition of O_2 (atm.)
7) P_{SO_2}(F) the initial feed composition of SO_2 (atm.)
8) P_{SO_3}(F) the initial feed composition of SO_3 (atm.)
9) C(2-10) the values of C(2)···C(NC)

Then at each value of contact time with corresponds to a print interval are printed out.

1) contact time (sec.)
2) PO_2 the O_2 composition in the gas stream (atm.)
3) P_{SO_2} the SO_2 composition in the gas stream (atm.)
4) P_{SO_3} the SO_3 composition in the gas stream (atm.)
5) PCONV the percent conversion
6) W/F the weight of catalyst used up to that time divided by the molar feed rate (g-sec/mole SO_2)

The operator has several options for running this program. If data switch 1 is off then the computer will start a new case as soon as it detects that the contact time for which calculations are being made is equal to or greater than TFV. If data switch 1 is on then the computer starts polling the other data switches. If they are all off, it will continue to wait until one of them is turned on or data switch 1 is turned off.

If data switch 2 is on then the computer runs the same case again at a new temperature. The data on the new temperature is laid out as on Card 4.

If data switch 3 is on the old case is rerun with a new TFV(n) [the value of TFV after the old case has been run n times under the control of data switch 3] given by:

$$TFV(n) = TFV(n-1) + TFV(1)$$

If both data switches 2 and 3 are on at the same time, switch 3 will be ignored until data switch 2 is turned off.

```
C     PROGRAM CONV - CALULATES THE PERCENT CONVERSION AND WEIGHT OF
C     CATALYST IN A CATALYTIC REACTOR AS A FUNCTION OF CONTACT TIME,
C     TEMPERATURE AND INITIAL FEED STREAM COMPOSITION.
C
C     BD=BULK DENSITY OF CATALYST BED (G./C.C.)
C     C(1) = TEMPERATURE(DEG. C.)
C     C(2-10)= MISCELLANEOUS CONSTANTS USED IN THE CALCULATIONS
C     EKP= EQUILIBRIUM CONSTANT FOR O2- SO2- SO3 EQUILIBRIUM.
C     FCONV= FRACTION OF SO2 CONVERTED
C     NC= THE NUMBER OF EQUATION CONSTANTS TO BE READ IN
C     PCONV=PERCENT OF SO2 CONVERTED
C     PO= INITIAL PARTIAL PRESSURE OF OXYGEN (ATM.)
C     P2=INITIAL PARTIAL PRESSURE OF SO2 (ATM.)
C     P3=INITIAL PARTIAL PRESSURE OF SO3 (ATM.)
C     PO2=INSTANTANEOUS PRESSURE OF O2 (ATM.)
C     PSO2=INSTANTANEOUS  PRESSURE OF SO2 (ATM.)
C     PSO3=INSTANTANEOUS PRESSURE OF SO3 (ATM.)
C     R=GAS CONSTANT (CAL./(MOLE-DEG. K.))
      T=CONTACT TIME (SEC.)
C     TFV=FINAL VALUE OF CONTACT TIME  (SEC.)
C     TII=INTEGRATION INTERVAL (SEC.)
C     TK= TEMPERATURE  (DEG. K.)
C     TP=PRINT INTERVAL (SEC.)
C     V= VELOCITY OF REACTION (MOL.SO3/(SEC.-G.CATALYST))
C     W= WEIGHT OF CATALYST CONTACTED/MOLAR FLOW RATE (G.-SEC./MOLE SO3)
C
      DIMENSION TITLE(20),Z(20),IN(5)
      COMMON C(10),V,PO2,PSO2,PSO3,EKP,TK
C
C     INITIALIZE VARIABLES AND CONSTANTS
C
      BD=0.75
      R=1.9872
  100 T=0.0
      TP=0.0
      V=0.0
      W=0.0
      FC1=0.
      L=0
C
C     READ AND PRINT CASE TITLE
C
  110 READ(2,1000)TITLE
      WRITE(3,1001)TITLE
C
C     READ IN INTEGRATION AND PRINTING VARIABLES
C
  120 CALL READP(4,Z,IN)
      TII=Z(1)
      TPI=Z(2)
      TFV=Z(3)
      TFV1=TFV
      NC=IN(1)
C
C     READ IN INITIAL FEED COMPOSITION
C
      CALL READP(3,Z,IN)
      PO2=Z(1)
      PSO2=Z(2)
```

Listing of Computer Program CONV

```
      PSO3=Z(3)
      PO=PO2
      P2=PSO2
      P3=PSO3
C
C     READ IN ANY CONSTANTS USED IN THE CALCULATION
C
  140 CALL READP(NC,C,IN)
      TC=C(1)
      TK=TC+273.16
      EKP=EXP(22600./(TK*R)-21.36/R)
  150 WRITE(3,1002)TII,TPI,EKP,TC,PO2,PSO2,PSO3
      WRITE(3,1003)(C(I),I=2,NC)
      WRITE(3,1004)
  160 TP=TP+TPI
  170 T=T+TII
C
C     SUBROUTINE REACV- CALCULATES VELOCITY OF REACTION
C
  180 CALL REACV
C
C     CALCULATE CONVERSION, NEW FEED GAS COMPOSITION AND W
C
      Q=V*TK*82.05*BD
      DELP=Q*TII
      PSO3=PSO3+DELP
      PSO2=PSO2-DELP
      PO2=PO2-DELP/2.
      FCONV=PSO3/(PSO3+PSO2)
      IF(L-1)181,183,183
  181 FC1=FCONV
      L=1
      GO TO 186
  183 FC2=FCONV
      X=W*(FC2-FC1)*1.7V
      FC1=FCONV
  186 IF(TP-T)190,190,170
  190 PCONV=FCONV*100.
C
C     PRINT OUTPUT
C
      WRITE(3,1005)T,PO2,PSO2,PSO3,PCONV,W,V
      IF(PCONV-99.)191,195,195
  191 IF(TFV-T)195,195,160
C
C     DATSW 1  OFF- GO TO NEW CASE, ON-POLL OTHER DATA SWITCHES
C
  195 CALL DATSW(1,JTA)
      IF(JTA-1)200,200,100
C
C     DATSW 2  OFF- CONTINUE , ON-RUN OLD CASE WITH NEW TEMPERATURE
C
  200 CALL DATSW(2,JTB)
      IF(JTB-1)210,204,210
  204 T=0.
      TP=0.
      V=0.
      W=0.
      FC1=0.
```

(Continued)

```
      PSO3=Z(3)
      PO=PO2
      P2=PSO2
      P3=PSO3
C
C     READ IN ANY CONSTANTS USED IN THE CALCULATION
C
  140 CALL READP(NC,C,IN)
      TC=C(1)
      TK=TC+273.16
      EXP=EXP(22600./(TK*RT-21.36/RT
  150 WRITE(3,1002)TII,TPI,EXP,TC,PO2,PSO2,PSO3
      WRITE(3,1003)(C(I),I=2,NC)
      WRITE(3,1004)
  160 TP=TP+TPI
  170 T=T+TII
C
C     SUBROUTINE REACV- CALCULATES VELOCITY OF REACTION
C
  180 CALL REACV
C
C     CALCULATE CONVERSION, NEW FEED GAS COMPOSITION AND W
C
      Q=V*TK*82.05*BD
      DELP=Q*TII
      PSO3=PSO3+DELP
      PSO2=PSO2-DELP
      PO2=PO2-DELP/2.
      FCONV=PSO3/(PSO3+PSO2)
      IF(L-1)181,183,183
  181 FC1=FCONV
      L=1
      GO TO 186
  183 FC2=FCONV
  185 W=W*(FC2-FC1)*1.7V
      FC1=FCONV
  186 IF(TP-T)190,190,170
  190 PCONV=FCONV*100.
C
C     PRINT OUTPUT
C
      WRITE(3,1005)T,PO2,PSO2,PSO3,PCONV,W,V
      IF(PCONV-99.)191,195,195
  191 IF(TFV-T)195,195,160
C
C     DATSW 1  OFF- GO TO NEW CASE, ON-POLL OTHER DATA SWITCHES
C
  195 CALL DATSW(1,JTA)
      IF(JTA-1)200,200,190
C
C     DATSW 2  OFF- CONTINUE , ON-RUN OLD CASE WITH NEW TEMPERATURE
C
  200 CALL DATSW(2,JTA)
      IF(JTA-1)210,204,210
  204 T=0.
      TP=0.
      V=0.
      W=0.
      FC1=0.
```

(Continued)

```
      L=0
      TFV=TFV1
      PO2=PO
      PSO2=P2
      PSO3=P3
      WRITE(3,1007)
      GO TO 140
C
C     DATSW 3  OFF-CONTINUE, ON-RUN OLD CASE CONTINUING THE INTEGRATION
C     FROM N*TFV TO (N+1)*TFV.
C
  210 CALL DATSW(3,JTC)
      IF(JTC-1)195,220,195
  220 TFV=TFV+TFV1
      GO TO 160
 1000 FORMAT(20A4)
 1001 FORMAT(1H1,20A4//)
 1002 FORMAT(3X,'INTEGRATION INTERVAL= ',F8.4,6X,'PRINT INTERVAL= ',
     1F8.4//3X,'K(EQ)= ',E12.5,6X,'TEMP.(C.)= ',F9.2//3X,'PO2(F)= ',
     2E12.5,3X,'PSO2(F)= ',E12.5,3X,'PSO3(F)= ',E12.5//)
 1003 FORMAT(2X,'C(2-10)= ',9(E12.5,2X)//)
 1004 FORMAT(1X,'TIME(SEC)',6X,'PO2',10X,'PSO2',10X,'PSO3',5X,
     1'FIRE.CONV.',8X,'W/F',10X,'VEL.'/)
 1005 FORMAT(2X,F8.4,2X,3(E12.5,2X),F7.2,2X,2(E12.5,2X)/)
 1007 FORMAT(/////)
      END
```

NOT REPRODUCIBLE

(Continued)

```
      SUBROUTINE REACV
C     DAVIDSON AND THODOS A.I.CH.E.J. VOL.10 568 (1964)
      COMMON C(10),V,PO,P2,P3,EKP,TK
      IF(C(2)-0.)20,10,20
   10 TK=TK*1.8
      PN=1.-PO-P2-P3
      R=1.986
      C(2)=EXP(44900./(R*TK)-34.51/R)
      C(3)=EXP(50400./(R*TK)-39.42/R)
      C(4)=EXP(57750./(R*TK)-46.62/R)
      C(5)=EXP(-44400./(R*TK)+44.13/R)
      C(6)=EXP(-36350./(R*TK)+29.77/R)
   20 V1=1.-P3/(P2*EKP*PO**.5)
      V2=(1.+C(3)*P2+C(4)*PO**.5+C(5)*P3+C(6)*PN)**2.
      V=C(2)*P2*PO**.5*V1/V2
      V=V/3600.
      RETURN
      END
```

Listing of Typical Subroutine REACV.

```
  EQUATIONS OF DAVIDSON AND THODOS
0.001 0.1 1.0 2
0.028 0.003 0.0
400. 0.0
```

Listing of Typical Input to Program CONV.

APPENDIX III

CATALYST DATA SHEETS

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APPENDIX III

INDEX

Catalyst Phase	Catalyst Base	Page No.
Solid	Vanadium	158
	Iron	186
	Chromium	191
	Platinum	194
	Carbon	205
	Manganese	208
	Miscellaneous	209
Liquid	Iron	213
	Manganese	214
	Miscellaneous	216
Gas	Miscellaneous	217

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CATALYST - VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1	V_2O_5	Solid-Gas												CA-50-16054d	Gaseous mix'ts. of varying concens. can be used without raising the V_2O_5 temp.
2	V_2O_5	"	250°C 300°C 360°C	Bi_2O_3-5% " "		V_2O_5-8% " "				3.25sec " "	7% " "		90.2% 95.5% 95.6%	CA-50-16059b	Conversions to SO_3 were much lower without the Bi.
3	Vanadium	"	430-530°C									20.2% 19.7% 19.5%		CA-53-13753h	Heat of activation was 36-39 Kcal/mol.
4	V_2O_5	"	365°C	Potash							0.35%		Complete	CA-55-14771e	Metallic oxides as absorbents and adsorbents were also reported.
5	V_2O_5	"	420°C	$K_2S_2O_7$					700cc/cc-catalyst		7%	10%	97%	CA-55-18033b	Reports how to prepare this catalyst.
6	V_2O_5				Diatomaceous earth conts. 5-20% Al_2O_3								Up to 98%	CA-57-P-11907a	Reports preparation of support material and catalysts
7	Vanadium	"												CA-57-16127h	Kinetic studies on the oxidn. of SO_2 on industrial vanadium catalyst.
8	V_2O_5	"	400°C	K_2O-11% Na_2O-5.0%		V_2O_5-7.2%							33%	CA-58-P-7413e	Preparation of catalyst is reported.
		"	500°C	"		"							82%		

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CATALYST - VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
9	Vanadium	Solid-Gas	460-550°C						11,000 m^3/m^3		7%	19.5%	85%	CA-59-3348a	Effect of water vap. and Fe_2O_3 on 'V' catalysts were studied.
10	Vanadium	"	420°C 450°C 460°C 470°C 500°C										86.3% 97.8% 97.1% 96.3% 94.3%	CA-59-7019f	Polish catalyst was compared with other 6 important catalysts No change in catalyst activity occurred after a 5-hr treatment at 700°C.
11	Vanadium	"	390°C 400°C 420°C	$KOH-K_2O$			0.55cc/g " "		hourly space vel=1900		7% " "	11% " "	22% 30.5% 50%	CA-59-P-7415b	Pore radii was 50-500A. Method of preparation of catalyst is also reported.
12	Vanadium	"	425°C											CA-60-2369a	Promoting action of Li, Rb, Cs, La, Ce, Pr and Nd were studied on BAV catalysts.
13	V_2O_5	"		$KHSO_4$-44%	N.Bolaks-48%	V_2O_5-8%								CA-60-2369e	The activity of series of catalysts were studied.
14	Vanadium	"												CA-60-2370d	Optimum shape and grain size for a V-catalyst.
15	V_2O_5	"												CA-60-2370z	Effects of alkali metal sulfates on the activity of V_2O_5 in the catalytic oxidation.
16	V_2O_5, K_2O	"		K_2O										CA-60-2372b	Different catalysts were prepared of these cmpds. and their activity and structure studied.

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CATALYST - VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
17	Vanadium	Solid-Gas	25-550 °C											CA-60-3527c	The effect of SiF_4 on V catalyst was studied. The degree of poisoning of catalyst by SiF_4 was determined.
18	V_2O_5	"	400-550 °C											CA-60-3527d	Effect of K_2O on the activity of V-catalysts were determined. Temp. at which catalyst becomes heated and loses its activity is decreased by the addn. of K_2O.
19	Vanadium	"									10%			CA-60-4843f	Series of catalysts were prepared to find an active catalyst with a suitable pore structure.
20	Vanadium	"	500°C								7.5%		88.68%	CA-60-15468c	Catalytic oxidation of SO_2 in a fluidized bed. With an increase of the SO_2 concn. from 7.5% the degree of oxidn. of it to SO_3 is reduced negligibly.
21	V_2O_5	"	485°C		Quartz, fused quartz, infusorial earth	V_2O_5-5.2 to 8.3%								CA-61-10082d	The nature of the effects of carriers was independent of structure and shape, and the activity depended on the resulting surface of catalyst.
22	V_2O_5	"	>400°C											CA-61-10336b	A table allows the reactor to be adjusted to changes of throughput and catalyst activity.

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CATALYST - VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
23	V_2O_5	Solid-Gas	520°C 542-63 °C											CA-62-5930f	Activation Energy 38.6 kcal/mole. Activation Energy 23.6 kcal/mole.
24	Vanadium	"	420°C		SiO_2								99%	CA-62-P-9848	
25	Vanadium	"									9.0-9.5 %		93%	CA-62-12778c	Bayer dual-catalyst process. Economic & tech aspects discussed.
26	Vanadium	"			natural SiO_2 infused earth, natural & molten quartz, silica gel, Al_2O_3, $BaSO_4$, porcelain, TiO_2	V_2O_5-5.22% to 8.30%								CA-63-4988h	Effects of carriers on the activity and properties of V catalysts were determined.
27	Vanadium	solid-gas	480-600°C						0.5m/sec		10-60%			CA-63-14366h	Optimum conditions for oxidation were determined.
28	Vanadium	"	500-590°C								7 %	12.5%	Decreased 78.5-67%	CA-64-1394c	Catalyst was poisoned in the presence of 0.3% HF and results studied.
29	Vanadium (V_2O_5-K-vanadate)	"	390°C -420°C		Disperse silicic acid						7%	20%	99%	CA-64-P-5805	Silica gel as support material was prepared and tested.

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CATALYST - VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
30	Vanadium	Solid-gas												CA-64-12212c	Differential reactor for kinetic studies of SO_2 oxidn. on a V catalyst is described.
31	Vanadium	"	400-570°C								16.1%	16.7%	98%	CA-65-323c	A 4-stage fluidized bed was tested for the oxidation of conc. SO_2
32	Vanadium	"	400-620°C								7%	19.6%		CA-65-5067b	In a differential reactor data on SO_2 oxin. were obtained which can be used in projecting and optimizing design of reactors.
33	V_2O_5	"		Ag_2SO_4	Silica									CA-65-8056g	Effect of nuclear rodiation on the activity of V-catalyst for SO_2 oxidn. was studied.
34	V_2O_5	"	370-400°C						0.8-1.1 m/sec		8.5-9.5%		max. 70%	CA-65-15538e	Partial oxidn. in a fluidized catalyst bed. The activity of catalyst dropped somewhat after 15 months of service.
35	Vanadium (V_2O_5)	"	380-560°C	K_2O Na_2O	Silica						10%	11%	<50%	CA-66-22608u	Promotion by K is greater than by Na by virtue of its position in the alkali-metal series. Pore dimensions discussed.
36	V_2O_5 (BAV	"	482°C	K (K/V=2.5/1)		V_2O_5=8.5%					8-23%	15-45%	80-96%	CA-67-15328v	The kinetics of SO_2 oxidn. was studied in a wide range of conditions using BAV catalyst

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CATALYST - VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
37	Vanadium	Solid-gas	360-450°C	No	Silica Gel								<10%	EI-52-1028	Mechanism of catalytic oxidn. of SO_2 with commercial V catalyst; kinetic study. Particle size = 10-14 mesh
38	Vanadium	"	380-600	C Na, K, RG, CS sulfates	None	16.8-33.9%			1 /min.		5%	20%	81.7-99.6%	EI-56-1045	V_2O_5 alone is poor catalyst for SO_2 oxidn. but when mixed with alkali metal salts good results can be obtained.
39	Vanadium (V_2O_5)	"	415-591°C	K_2O 8-10.4%	70% silica kieselguhr or cellite	V_2O_5 6-9%					8%			EI-58-1228	Effect of physical & chemical factors in catalytic oxidn. of SO_2, including poisoning of catalyst, catalyst placing and converter design.
40	Vanadium (V_2O_5)	"	430°C-511°C	6.3-10.6% K_2O opt. 9.5%	silica	6.7-7.7% opt. 6.7%			linear vel=24 cm/sec.	0.09-0.43sec. opt.0.19 sec.	0.03-0.27%	1.85-6.8%	84-98%	EI-59-482	Different composition of V_2O_5 catalysts were studied for the catalytic oxidn. of SO_2. Catalyst prep. described. Bulk density 0.62g/cc.
41	V_2O_5	"	543,672, 722°F	K_2O 9.0= 11.0% Fe 0.5%	Alumina-Silica Spheres (3/16"Dia.)	7.35-9.35%			(high)				15%	EI-65-2465	Kinetics of catalytic oxidn. of SO_2 were studied in differential bed reactor. Bulk density 0.70g/cc.
42	V_2O_5	"												CA-57-7965c	Reaction rates of oxidn. of SO_2 with 4 kinds of feed gas composition.
43	Vanadium V_2O_5	"	400-420°C		Silica from water glass			100-200 m^2/g					99.2-99.5%	CA-57(P)-6670d	Preparation of catalyst described.

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CATALYST - VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
44	Vanadium	solid-gas	530°C											CA-57-3247g	Advantages of fluidized-bed catalysis.
45	V_2O_5	"		Na_2SO_4 iron oxides										CA-54-27351	High temp. corrosion by V_2O_5 is decreased by the addn of dolomite and $(NH_4)_2SO_4$.
46	V_2O_5	"	700°F	K_2O-10% P_2O_5-1%	Silica-alumina	V_2O_5-7.5%			14,320 ft3/min		12%	9%	95-99%	CA-66-P-4550	Oxidation of SO_2 to SO_3 with low ignition catalyst is shown.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
47	Vanadium Zeolite	Solid-Gas			Zeolite									CA-25-P-940-1	Gas containing SO_2, O and catalyst poison (e.g. HCl) passed over Pt-free V-zeolite at elevated temperatures.
48	V_2O_5	"	400°C		Silicic acid				50cc/sec.		5.2-7.0%		97.85-99%	CA-24-5585-4	Greater catalytic action than V-zeolite.
49	V_2O_5	"			Stannic Hydroxide gel									CA-25-P-565-3	Preparation of catalyst described.
50	Vanadium cmpds. capable of yielding vanadyl sulfate	"	400°C	Salts of Cu, Bi or Mn	Pumice, kieselguhr, diat. earth or silicic acid								94-95%	CA-25-P-1344	Preparation of catalyst described. Treated with acid gas such as SO_2 in the cold. Immune to poisons.
51	Alkali metal vanadate or vanadite, vanadyl salts, vanadal sulfate or NH_4 vanadyl oxalate	"	450-500°C		Ground silica, siliceous brick, sand or kieselguhr and wet silica gel									CA-25-P-1045-2	Preparation of catalyst described pellets may be formed.
52	Vanadic Anhydride, metal vanadate or sol. vanadate solution.	"			Finely divided indifferent support and binder.									CA-25-P-2817-2	Preparation of catalyst described. Agglomerate treated in the cold with a reducing gas until V is completely reduced.

CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc	O_2 Conc	Conversion Efficiency	Reference	Remarks
53	Sn or Bi vanadate	"			Pumice, as best a, silica ge, alumina gel or $MgSO_4$								------	CA-25-P-4095	Preparation of catalyst described.
54	Sn vanadate	"	Activat 300-350°C Opt. at rate-490°C						*Space velocity Air 225-1500 SO_2 5-112				*58.3-98.7%	CA-26-664-5	At high SO_2 rates or too low temp. obstructive adsorption may occur. Insensitive to as poisoning.
55	Vanadium catalyst	Solid Gas			non-permuto-genetic contact mass conta. active silicate									CA-27-P-11098	Elevated Temp.
56	V-compd.	"			Siliceous diluent and a silica hydrogel									CA-27-P-22595	
57	Vanadium	"			Diatomite brick fragments									CA-27-P-3043-3	Catalyst described as chemically combined Ag and V on an alkali-forming metal.
58	V_2C_5	"	400°C		$Sn(OH)_2$								99%	CA-29-2668-7	Preparation of catalyst described. Activity of catalyst due both to an adsorption process and to partial reduction to V_2O_4, which acts as an O carrier.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
59	Vanadium catalyst	"	440-500°C		SiO_2						39%	61%		CA-29-2668-8	Oxidation per min and per g. of catalyst is 5 times as rapid as in a gas contg. 7-8% SO_2, 19% O_2 and 73% N_2. Preparation of catalyst described.
60	Na Vanadate	"		K_2SO_4	Kieselguhr and gum tragacanth									CA-29-P-56106	Preparation of catalyst mixture described. Can be granulated or pelleted; procedure described.
61	V_2O_5	"	360-520°C		SiO_2									CA-29-7775-6	Effect of varying porosity at different temperatures described with increasing porosity the temp. of the max. yield of SO_2 is lowered. Activation energies are the same for different porosities but increase at lower temp.
62	Na Vanadate	"			Kieselguhr and gum tragacanth									CA-30-P-19554	Preparation of catalyst described.
63	V_2O_5 (from K_3VO_4	Solid	458-498°C	K_2SO_4	Silica Gel									CA-30-P-31825	Preparation of catalyst described.
64	Na Vanadate	"			SiO_2									CA-30-3306-2	Catalytic activity with and without adding of SiO_2 observed. Dissociation pressures of sodium vanadate and oxidation of SO_2 was measured at different temps.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc	Conversion Efficiency	Reference	Remarks
65	V_2O_5 (from V containing ore	"		Na_2SO_4 or K_2SO_4	One more 90%	Less than 10%								CA-30-P-5740M	Treatment of V-containing material, to render it catalytically active, described.
66	V_2O_5 (from K_2VO_3	"			Kieselguhr									CA-32-P-10621	Method of manufacturing catalyst material described.
67	Vanadium catalyst	"	425°C											CA-34-3025-8	Fouling of catalyst surface by $Fe_2(SO_4)_3$ investigated.
68	V_2O_5	"	450°C	$K_2S_2O_7$	Silica									CA-34-6156-6	Mechanism of oxidation of SO_2 postulated.
69	V_2O_5	"		K_2SO_4, Na_2SO_4 or Li_2SO_4										CA-34-7169-4	Reaction accelerated due to lowering of melting point of V_2O_5 by ca-catalysts.
70	V_2O_5	"		K_2O or K_2SO_4	SiO_2					12-16hrs.	5%	17%		CA-34-8285-5	Activity of V_2O_5 found to be less than that of KVO_3, $NaVO_3$, or $Ba(VO_3)_2$. Reaction of V_2O_5 with SO_2 to give vanadyl sulfate described.
71	V_2O_5	"				5-6%								CA-37-2145-7	Wt % V_2O_5 catalyst and rate of passage of gases effects on percent of conversion given.
72	V_2O_5	"												CA-38-910-9	Mechanism of the reduction of V_2O_5 to V_2O_4 or V_2O_3 during oxidation of SO_2 given.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
73	V_2O_5	Solid-Gas		KOH	Kiesel-guhr, clay									CA-42-6496e	Preparation of non-swelling catalyst and method of activation described.
74	Ag metavanadate, V_2O_5, V_2O_5 + Fe, Cr_2O_3	"		Fe, Ca SnO_2	Silica gel and infusorial earth " SiO_2 with 10% gypsum						Opt 7-8% Opt 7-8%			CA-42-8058h	Oxidation studied with different catalysts, temps, space velocities, and compositions of gases. The Ag vanadate and the V_2O_5 + Fe and Ca were best.
75	V_2O_5	"	420-480°C	Fe, Sb_2O_3										CA-43-2744e	Degeneration of catalyst investigated.
76	V_2O_5, *Pt or V_2O_5 + Pt	"			Sillimanite, bonded by silicate									CA-43-8074e	Method of preparing catalyst described.
77	Vanadium catalyst	"	410°C 414°C 405°C 420°C 438°C 392°C 388°C 423°C 420°C 410°C 394°C	K_2O BaO					Lin. vel. 0.15m/sec		7% 50% 75% 90% 95% 50% 25% 7% 8.5% opt14% 66.7%	19.6% 10.5% 25% 10% 5% 50% 75% 11% 12.5% 18% 33.8%		CA-43-8251g	Temperatures given are the lowest temperature of the gas mixture that causes the temp of the contact catalyst to rise spontaneously by 10°. The extinction temp. on cooling is lower than the heating-up temp. The catalytic oxidation of SO_2 takes place entirely at the surface and does not extend into the gas phase.
78	V_2O_5	"	*425-		*Alundum tubes	*6.5-7.25%	*47%		*4.0-37.3 cm/sec.		*7.8%	*19.4%	*<88%	CA-46-3841g	Reaction kinetics discussed for tubular reactor.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
79	V_2O_5	"	*800-1000°F											CA-46-P-6876a	Fluidized powdered catalytic material described.
80	KVO_3	"			Kieselguhr				*0.65-1.6 cm/sec.		*6%	*15%		CA-46-P-9902b	Apparatus using fluidized catalyst and mechanical vibrations described. *Grain size 0.3-0.2mm.
81	Vanadium catalyst										7%			CA-47-P-6714a	Effect of vibration on reaction at various rates of flow described.
82	V_2O_5	Solid-Gas	*440-470°C	*12-22% K_2O	*40-55% SiO_2 Pellets	*7-12% V_2O_5			*250C 1/1-hr		*6%		*82-92.5%	CA-48-P-9586e	Preparation of catalyst described.
83	Commercial V_2O_5	"	360-450°C	2% Na	Silica Gel	12% V_2O_5					17-80%	4-18%	*~50%	CA-48-80031	Reaction rates determined and mechanism given.
84	Vanadium catalyst	"		BaO										CA-32-3687-1	Poisoning of catalyst by adsorption of HF investigated. Regenerated calayst showed increased activities.
85	Vanadium catalyst	"	*508-536°C	BaO	Al_2O_3		*60%	*4.8-258 cm^2/g	400-700		*4-7.4%		*37-78.8%	CA-48-13386f	Rate constant dependence on surface area of catalyst particles demonstrated.
86	V_2O_5	"	450°C	TiO_2		Up to 25% (Max act. at 8% V_2O_5)								CA-49-10717g	Preparation of catalyst described. Catalytic activity examined at various V_2O_5 concentrations.

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Catalyst-Vanadium

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
87	V_2O_5	"	360-630°C											CA-50-3939c	When V_2O_5 is reduced by SO_2 at low temp. $VOSO_4$ is first formed, changing to V_2O_4. At higher temps. V_2O_5 is formed directly.
88	V_2O_5	"												CA-50-6164b	Hydrodynamics of gas flow in fluidized catalyst system calculated.
89	V_2O_5	"	250°C 300°C 360°C 380°C 425°C 455°C	4% Bi_2O_3 " " Without Bi " "	Be water glass(17% SiO_2)	8% V_2O_5 " "				3.25 sec " " " " "	7% " " " " "		90.2% 95.5% 98.8% 25-30% 66.0% 98.6%	CA-50-P-10059b	Preparation of the Bi containing catalyst described.
90	Vanadium catalyst	"	*420-550°C	*K_2O	*Silicate *Quartz glass 1-2 mm dia.						*5.3%	*19.9%		CA-51-7818f	A discontinuity on the curve of log K vs 1/T is related to the conversion of the catalyst to the inactive V sulfate.
91	V_2O_5	"	*380-450°C	*K_2O *(K_2O/V_2O_5 =4.5/1 to 5.4/1	Kieselguhr 50%	6-7.5%			2500 l per l catalyst space per hr.		*6.5-9.6%	*11.3-14.4%	*36-99.6%	CA-51-P-8396d	Method of preparing catalyst mixture is described. *varying $K_2O : V_2O_5$ ratio for lower initiating temps.
92	V_2O_5	Solid-Gas	445-60°	Na_2O 10.01 SO_4 15.62 K_2O 3.19	SiO_2 58.10 Al_2O_3 7.16	1/2 O_5 5.92				4.2-9.2 sec.	7%		98%	CA-51-124451	Procedure for preparation of catalyst described.
93	Commercial V_2O_5	"	*374-433°C	*K_2SO_4 33%	*Silica Gel	*10% V_2O_5			*mass vel. = 3.5-50.0 lb/hr-sq.ft.		*0.2-8.0%			CA-51-17023a	Comparsion between fixed and fluidized catalyst beds made. Fluid bed is 3.59 times more effective. (*catalyst 60-80 mesh).

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	Catalyst	Type of Catalysis	Temp	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc	O_2 Conc	Conversion Efficiency	Reference	Remarks
94	Vanadium catalyst	Solid-Gas			Kieselguhr (Types LM and SK)									CA-52-14944a	Influence of pore-size and pore distribution of carrier on activity of catalyst is discussed.
95	V_2O_5	"	380-480°C opt.-less than 440°C											CA-52-16197f	Dependence on temp of the valence of V present is discussed.
96	V_2O_5	"	390-490°C	K_2SO_4										CA-52-17637t	Phase condition of active component (proposed to be V_2O_5-K_2SO_4 and V_2O_5-$K_2S_2O_7$) at temp between 390-490°C described.
97	V_2O_5	"									0.11-0.17%		98%	CA-53-7524g	Four V_2O_5 catalysts were compared. Contact time, SO_2 and O concentration were studied.
98	V_2O_5	"		K_2O 5.5-8% Na_2O 1.25-1.75%	SiO_2 52.5-62.5%	V_2O 3.5-7.5%								CA-53-P-11781a	Preparation of catalyst described.
99	V_2O_5	"	380-550°C	K_2O Na_2O							7%			CA-53-13755a	2-step reaction tubes used. The rates of reaction at each stage of reaction and total rate were calculated and discussed.
100	V_2O_5	"	390-475°C 450-525°C	K_2O-Na_2O Na_2O										CA-53-13755d	Kinetic equations and activities given.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
101	Vanadium Catalyst	Solid-Gas	*250-500°C	*Fe_2O_3 FeO-17.4% (u.c.-o)	Al_2O_3 *Aluminum gel Al-O-3.24% SiO_2 50-80%	*V(as V_2O) 7.2-13.5%	*59-75Å	*32-47 m^2/g	5200/hr		*0.5-7.0%		*up to 93%	CA-53-20624g	Al_2O_3 increases the thermal resistance of the catalyst by stabilizing the physical structure. *Catalyst Grain size 1-2mm.
102	Vanadium Catalyst	"	380-550°C								2-18%		80%	CA-54-3877c	Calculation of velocity constants of oxidation described.
103	K Vanadate	"	485°C		SiO_3 or Al silicate								92.7%	CA-[illegible]8533 g	Method of preparing spherical catalyst bodies described.
104	Vanadium Catalyst	"	440-520°C						0.4-0.9 m/sec. *Vol 1500-29000 *optimum 1700	*0.07-0.15 sec	*7-30%	*10-70%	*80.6-98.1%	CA-54-219761	Optimum temp variation with SO_2 concentration and variation of yield with height of fluidized bed, catalyst particle diameter, and volume velocity is discussed. *Particle size 0.5-1.5mm.
105	Vanadium catalyst *(BAV and SVD)	"	500°C		*Cylindrical Granules				0.1-2.5 m/sec.		7%		*80-90%	CA-55-3019e	Effect of particle size on activity in fluidized bed discussed. Rate constant approx. 30/sec for particle diam <1.5mm, decreasing rapidly for particles >1.5mm in diam.
106	Vanadium catalyst	"	450-490°C						0.5-3.5 l/min.		2.7-7.0%		10-70%	CA-55-3132e	Catalyst particle size 0.78 and 1.mm. Activity always increased when bed became fluidized regardless of SO_2 concentration and temp.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
107	V_2O_5	Solid-Gas		Rb_2SO_4 $Rb_2S_2O_7$ Cs_2SO_4 $Cs_2S_2O_7$	SiO_2	2-10%								CA-55-P-8789a	Method of preparing catalyst described.
108	V_2O_5	"		Rb_2SO_4 Cs_2SO_4										CA-55-23009h	Method of fusing promoters and catalysts described. Promoters mentioned gave 9 times the catalytic activity given by K_2SO_4.
109	Vanadium catalyst	"			Kieselguhr									CA-55-23011c	Catalytic oxidation studied by using differential thermal analysis under controlled atmospheres of reactants.
110	V_2O_5	"	485°C	0.1 mole Li_2SO_4 0.1 mole Na_2SO_4 0.1 mole K_2SO_4 0.1 mole Rb_2SO_4 0.1 mole $Cs_2S_2O_7$		1 mole V_2O_5								CA-56-9468c	Promoting action compared for different alkali metal sulfates using O isotopes.
111	Vanadium catalyst	"	450°	With and without Na_2SnO_3	Al_2O_3-SiO_2								97%	CA-56-14972f	4 methods of catalyst preparation were compared.
112	"BAV" V_2O_5	"									7-11%			CA-57-3247b	Pilot-plane equipment demonstrating the advantages of the fluidized bed described.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
113	V_2O_5	Solid-Gas	370°C *388-445°C	$KHSO_4$ Ag_2SO_4 $(NH_4)_2SO_4$ *$K_2S_2O_7$ *$Na_2S_2O_7$ *WO_3	*SiO_2	*5.8%	Pore rad 80Å Inner surf. 420 m/g Pore vol 1.85cc/g						84%	CA-57-P--11906d	Method of preparing catalyst described.
114	Vanadium catalyst	"	500°C						0.17-3.3 m/sec.		7-30%		80%	CA-57-16128a	Industrial scale fluidized bed described. Catalyst particle sizes of 0.127-4.5mm compared.
115	V_2O_5	"	450-60°C 390-410°C		*Kiesel-guhr						9.3%		99.6-99.8	CA-58-278b	Multistage process described.
116	"BAV" V_2O_5	"							3.2-8.9 cm/sec.						Longitudinal mixing and wall effects were investigated using small glass reactor.
117	V_2O_5	"	*Wear Resistant Ignition Temp=370°C	K_2O 3.8%		V_2O_5 6.1%	600-800Å *BAV= 1300-1500Å		*3500-4500/hr *0.31-0.39m/sec		*7.5-9%	*13.3-11.8%		CA-62-14214c ET(1966)351	Wear-resistant V_2O_5 catalyst compared to "BAV" catalyst in fluidized bed. *Grain size 1.5mm dia.
	"BAV" V_2O_5	"	*BAV= 410°C	K_2O 5.4%		V_2O_5 6.1%	1300-1500A°		1200/hr pilot plane						
118	V_2O_5			Na_2O	Al_2O_3-SiO_2									CA-63-7928h	Method of catalyst preparation described. Various mixtures compared.
119	V_2O_5	"	450-500°C										unmilled 35-38% premilled 86%	CA-63-17197f	Effect of pre-milling on activity described. Pure 60mμ V_2O_5 was the starting material.

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	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
120	KVO_3			K_2SO_4	Al_2O_3-SiO_2									CA-65-9854d	Structural characteristics of catalyst surface discussed.
121	V_2O_5		400°C		Kieselguhr	V_2O_5 7.2%							97%	CA-65-P-11835f	Sulfuric acid produced at max load capacity of 10 kg H_2SO_4/ Kg catalyst/ day.
122	Vanadium catalyst	Solid-Gas	485°C		Calcined hydrogel						10%	20%	93%	CA-65-P-19352d	Preparation of catalyst with addition of natural or synthetic fiber to increase porosity and resistance to abrasion is described.
123	V_2O_5	"	400°C	K_2O	SiO_2	Moles V_2O_5 per mole K_2O= 1/3							ground 70.5% unground 20.5%	CA-66-79958n	SiO_2 carrier ground in a vibration mill.
124	V_2O_5	"	380-450°C										95%	CA-66-87175v	SO_3 precipitated from flue gas as $(NH_4)_2SO_4$.
125	V_2O_5	"	340-410°C	K_2SO_4					30m³/hr space vel = 1000-8000		0.2% *-2.5%	2%	85%	CA-68-P-42924p	SO_3 recovered from flue gas as $(NH_4)_2SO_4$ (99% pure).
126	"SVD" com V-catalyst	"	460-520°C		Kieselguhr				1000-2000 ml/min.		7-10%	11%		CA-68-43558j	Kinetics measurements made in a differential reactor described in a supplemental reference.
127	V-Catalyst	"												CA-39-3997[5]	Equations and theoretical discussion of the reaction are presented and V catalyst compared with Pt catalyst.

CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
128	V-Catalyst *($2SnO_2 \cdot K_2O \cdot V_2O_5 \cdot 8SiO_2$)	Solid-Gas	>440°	*SnO_2 K_2O BaO										CA-28-4181[8]	The influence of contact time, composition of gas mixture and temperature on the oxidation rate is studied. Results compared to those with Pt.
129	V-catalyst	"												CA-28-P-2478[7]	Apparatus described. V-catalyst compared with Pt as to capacity.
130	Ca-V and Fe-Sb-V-catalysts	"		Ca Fe-Sb										CA-37-6416[7]	Properties of catalysts studied.
131	V_2O_5	"	450-800°C						$15m^3/hr$		66%	34%	60%	CA-41-P-841d	Method of preparing SO_3 described.
132	V_2O_5	"												CA-42-3918d	Data summarized on particle size and porosity and the calculation of overheating coefficients for several catalysts used for the oxidation of SO_2.
133	V_2O_5	"	~520°C										50%	CA-60-4851a	The effect of pressure (4 atm) on the catalytic oxidation of SO_2 was investigated. Pressure has a small influence on porous carrier catalysts.
134	V-Catalyst	"		Zeolite	Kieselguhr									CA-22(P)-1018[9]	Method of preparing contact mass is described.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
135	Vanadates or vanadites of Fe, Cu, Ag, Ni, Co, Ti, Zr, Ce, Al, Ca, Cd, U, Cr or Mn	Solid-Gas	*430-550°C	*Alkali Metals	Zeolite containing Al, Re, Cd, Zr, Zn or Ti *(33° Be' Waterglass Celite, Kieselguhr, etc.	*5-10%					*4-6%		*96-98.5%	CA-23(P)-486[5]	Details of catalyst preparation are given.
136	Zeolite contain-V.	"	*450-600°C	Zeolite *containing K	Zeolite *Containing SiO_2 and catalytically active metals.	*Zeolite contain-V + other catalytically active metals.					*7%			CA-23-(P)-940[2]	Preparation of catalyst described.
137	V-compds.	"			Kieselguhr and SiO_2									CA-25(P)-1045[7]	Support material described.
138	V-silicate	"			Kieselguhr pumice or glaucosil									CA-26(P)-2022[6]	Method of catalyst preparation described.
139	V-catalyst *(followed by Pt catalyst)	"	*700-1200°F		*V-pellets Pt-Abestos									CA-27(P)-5488[3]	Catalytic process renders impurities such as Fe and F harmless, which are poisonous to Pt catalysts.
140	V-Catalyst	"												CA-31-3217[9]	Kinetics of catalysis compared with that of Pt.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
141	V-catalyst	Solid-gas	470°C								5-11%	16%		CA-32-1963[3]	Optimum concentration of SO_2 in sulfuric acid production discussed.
142	V_2O_5	"		K_2SO_4 Na_2SO_4										CA-35-3883[4]	Mechanism of oxidation on oxide catalyst discussed.
143	V-catalyst	"												CA-40-2943[5]	Kinetics discussed.
144	V_2O_5	"												CA-57-1101	Mechanism discussed.
145	K Vanadate	"												CA-24-3089[2]	Preparation of catalyst described.
146	V_2O_5	"		$CuSO_4$ $Fe_2(SO_4)_3$ $BaCl_2$	MnO_2, infusorial earth porclain, asbestos, glass, quartz sand								up to 97.8	CA-29-2699[5]	Effect of promoters and carriers on catalytic efficiency discussed.
147	V_2O_5	"	400-550°C	K_2SO_4	SiO_2									CA-35-3396[7]	Effect of various amounts of K_2SO_4 and SiO_2 on catalytic activity of V_2O_5 is discussed.
148	Ba-Al-Vanadate	"	465-550°	BaO Al_2O_3										CA-53-7743h	Effect of S concentration in gas on catalytic activity studied.
149	Monsanto V_2O_5	"	>435°											CA-54-30321	Reaction velocities calculated.

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc	O_2 Conc	Conversion Efficiency	Reference	Remarks
150	V_2O_5	Solid-	>500°C>											CA-54-11672d	Results of thermographic study presented.
151	V_2O_5	"	420-525°C	Rb_2SO_4 Cs_2SO_4 *4-6%		6%				*0.435 sec.	*10%	*18%		CA-54-11672e	Effect of alkali-metal sulfates on catalytic activity studied. *Velocity constant 9 times greater than with K_2SO_4. *kinetics discussed.
152	Ba-Al-V	"	>500°C>	BaO Al_2O_3										CA-54-21961f	Particle size 1.5-2.0mm.
153	V_2O_x	"	470-608°C					*<0.05 m^2/g						CA-55-15139e	Semi-conducting properties discussed.
154	V-catalyst	"	400-500°C											CA-56-2025h	Mechanism discussed.
155	V_2O_5	"		Al_2O_3										CA-58-960d	Rise of resistivity of catalyst due to Al_2O_3 explained. Mechanism of SO_2 oxidation derived.
156	V_2O_5	"	400-430°C											CA-58-1138d	Design of reactor described.
157	BAV	"	530°C	BaO-Al_2O_3									78.5%	CA-59-3348b	Poisoning by As_2O_3 discussed
158	V-catalyst	"			Silica Gel			0.5-21.5 m^2/g			75%	25%	98.4%	CA-59-4581e	Chromatographic methods used to test catalysts.
159	K-Vanadate	"		K_2SO_4	Silica gel alumino-silicon gel									CA-60-2368f	Method of preparing catalyst described.
160	BAV	"	25-550°C											CA-60-3527c	Poisoning of catalyst by SiF_4 studied.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
161	K-Vanadate	Solid-Gas		K_2SO_4	Silica alumina-silicate VKhK(?)									CA-60-11412h	Production of catalyst described.
162	BAV SVD	485°C -700°C									10%	18.9%		CA-61-330e	Contamination of catalyst by carbon black examined. At high temp. (700°C) C causes irreversible contamination when its amt >5%.
163	V_2O_5	"	485°C		Quartz, fused quartz, marchalite, and infusorial earth	5.2-8.3%								CA-61-10082e	Data correlated with the average particle size and specific surface area of the catalyst supports.
164	V_2O_5	"			Al_2O_3 K_2O									CA-61-P-11376c	New catalyst described.
165	V-catalyst	"											99.6%	CA-62-10104f	Bayer double-contact process described.
166	V-catalyst	"	485°C						$2000hr^{-1}$					CA-63-7925d	Effectiveness of various catalyst shapes investigated.
167	V_2O_5	"	500°C	11.5% K_2O	SiO_2 part. size 0.5-1mm	8%								CA-63-P-17527h	Preparation of catalyst beds described.
168	V_2O_5	"	370-400°C											CA-64-P-1392b	Design of equipment for SO_2 removal from flue gas described.

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	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
169	V_2O_5	Solid-gas	480-550°C			Pure V_2O_5								CA-64-2784g	Activity of pure V_2O_5 from different sources studied.
170	V-catalyst	"	440°C											CA-64-7690c	Design of equipment described.
171	V-catalyst	"		$KVO_3+K_2SO_4$	Alumino-Silicates									CA-68-63031k	Structure of wear resistant catalyst studies.
172	V_2O_5			K_2CO_3	K-silicate silica gel									CA-68-P-63101h	Shaped catalysts described that have higher activity and longer life.
*174	V_2O_5	"	450°C	TiO_2										CA-62-3445f	Catalytic activity accelerated by electromagnetic radiation.
175	POV (Ba·Sn·V	"	>440°C	SnO_2 BaO K_2O		V_2O_5								CA-29-6371[3]	Use of Barium Tin Vanadate Catalyst described.
176	V_2O_5 ($2K_2O \cdot BaO \cdot 0.5\ Al_2O_3 \cdot V_2O_5 \cdot 12\ SiO_2$)	"	470°C								4-23%	6.5-40%	21-91%	CA-32-1055[2]	-
177	V_2O_5	"	420-554°C	K_2SO_4	Kieselguhr						k-6%	4-20%		CA-51-6100b	Grain size 0.67-1.38mm.
178	V_2O_5	"	240-383°C	10% K_2O Ni	Kieselguhr	8.5% V_2O_5							<22%	CA-61-8942a	Interfacial compositions were calculated and used to show that the apparent rate-controlling step involves the surface reaction between chemisorbed SO_2 and chemisorbed atomic O to form chemisorbed SO_3 and a vacant site.

CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
*179	V_2O_5	Solid-G&s	395-450°C	K17% Ca 5.1% Na 0.9% K 9% Na 0.15% K 10% Na 2.9%	Silica	V_2O_5 8.2% V_2O_5 7.1% V_2O_5 6.8%								CA-68-81692f	Mechanism and kinetics of SO_2 oxidation on Alkali-promoted catalysts described.
180	V_2O_5 Fe_2O_3 Pt.	"	450-500°	K_2O Ma_2O also Cu, Co, Ni, Cr, Al, W, U, Ca ions	SiO_2				12-1/hr		8%		66-98%	CA-24-3089²	Activity of various combinations of catalysts and promoters investigated. Method of preparing catalysts described.
*181	V_2O_5	"	440-580°C						10000 m^3/hr	Total (5 stages) 1.00 sec.	5-7%		97%	EI-61-1699	Operation of converter for production of H_2SO_4 described, employing 5 catalyst layers. Capacity: H_2SO_4/cat-24hr=5.7 tons/ton.
*182	V_2O_5	"		10.6% K_2O	Kieselguhr	7.7%					6-12%	5.2-13%	97%	CA-50-9211	Review of kinetics, mechanism and types of converters. Data given for experiments with two stage converter.
183	Ag vanadate	"	325-550°C	Ag					150-700				57-97%	CA-23-1725	Activators in the reaction using V_2O_5, Fe_2O_3, TiO_2, WO_3 and Cr_2O_3 as catalysts is discussed.
184	V_2O_5	"	475-575°C			100%					4-40%	5-40%	28-71%	CA-41-6121f	Kinetics investigated.
*185	BCR vanadia catalyst	"	650-800°F						1300-3400 cc/min 1.5-3.1fps	0.008-0.039min.	0.3%		58-61%	CA-65-2892b	Problems associated with removal of SO_2 from flue gas are discussed.

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	Catalyst	Type of Catalysis	Temp	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc	O_2 Conc	Conversion Efficiency	Reference	Remarks
*186	Industrial Vanadium catalyst	Solid-	442-600°C								8%	12%	97%	CA-55-13944h	Optimum process conditions for a multistage reactor discussed.
*187	Vanadium catalyst	"	380-560°C (560opt)								8%		96%	CA-48-4121	0.93 tons catalyst required per 50 tons H_2SO_4 produced in proposed contact-process converter design.
188	V_2O_5	"	420-550°C	Exchangeable bases							7-9%			CA-23-P-1998[2]	Preparation of catalyst mixtures described.
*189	Vanadium catalyst	"	400-550°C						50ft³/min per ton H_2SO_4 produced		6-10%		99.1%	CA-68-P-4523	117-l./short ton H_2SO_4/day necessary in described 2-stage process.
*190	V_2O_5	"	330°C	K_2O 16.5% SO_3 27.3%	SiO_2 39.6	V_2O_5 7.1%			1050		0.32%		98%	CA-54-13509f	Bench scale investigations of SO_2 removal described.
*191	V_2O_5	"	400-600°C	K(3.4-7.6%		V(2.2-5.5%)					9%			Journal Article #231	Kinetics and mechanism of reaction catalyzed by vanadium oxides dissolved in potassium pyrosulfate are investigated.
*192	V_2O_5 (Potassium vanadite)	"			Hydrous gel or fuller's earth Kieselguhr, etc.								98.5%	CA-28-P-867[8]	Several examples of catalytic mixtures are described.
*193	Vanadium catalyst	"	600°C								6.5%			CA-46-P--11608d	Description of apparatus for contact process of H_2SO_4 production described.

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CATALYST-VANADIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
*194	Nissan Vanadium catalyst	Solid-	400-570°C	K_2O		V_2O_5			Space gel = 600-40,000		7%	10-19.5%			Studies made at atmospheric and increased pressures on reaciton velocities.
*195	V_2O_5	"												CA-53-13753-f	Thermodynamics of V_2O_5, Pt, N_2O_3, Fe_2O_3 catalytic oxidation compared.
*196	BAV catalyst	"									10%	18.9%		CA-60-1147c	Calculation of rate constants discussed.

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CATALYST - IRON

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1	Steel	Solid-gas							150 ml/min	1-48 hrs	0.2-6%		7-10%	CA-43-5910g	Coating steel with Al considerably reduces the rate of catalytic oxidn. And material.
2	Fe_2O_3	"	580-635°C *375-635°C											CA-43-5395d	Maximum catalytic activity is between 580-635°C
3	Iron oxide	"												CA-57-4090f	Catalyst could be regenerated in the fluidized bed at 600-700°C.
4	Fe_3O_4													CA-58-965b	Catalytic activities of metal oxides for the oxidn. of CO. Deviations were observed in the application of method for the oxidation of SO_2.
5	Iron	"									12%	18.5-19%		CA-61-9185d	Utilization of iron catalyst in the contact chamber process.
6	Iron oxide	"	680-700°C								12%		36-40%	CA-65-16553d	Oxidn. of SO_2 with a fluidized bed of Fe oxide in contact process.
7	Iron *material	"							*LIN=0.6 m/sec *VOL=2000-8000/hr	*0.14-0.27 sec		9%	*28-45%	EI-65-284	Iron catalyst for the oxidn. of SO_2, may be used for contact tower process in manufacture of sulfuric acid. And material.
8	I on	"	*610-730°C						*0.975 m/sec		*12%			EI-66-3002	Problems of using iron catalyst in contact tower process. Equations are derived for kinetics of oxidn. of SO_2. And material.

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CATALYST-IRON

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc	Conversion Efficiency	Reference	Remarks
9	$Fe(OH)_3$	Solid-Gas	125-130°C		Pumice asbestos $BaSO_4$ paper or marl				31/hr		10%			CA-31-6830[9]	Choice of support material with respect to gas velocity discussed.
10	Fe_2O_3 Fe_2O_3-CuO	Solid-Gas	350-600°C			Pure Fe_2O_3 1-70.0% CuO			100-200 (vols gas/unit Vol cat.-hr)		7% 7%		40-73.4% 40-73.4%	CA-37-2145[1] CA-37-2145[1]	Variation of activity of catalyst with variation of flow rate temp. and % CuO measured at low temps (350-400°) and high CuO content (40-70%) the activity is 6-20 times that of pure Fe_2O_3.
11	Fe_2O_3	Solid-Gas	640-80°C											CA-40-5211[9]	Rate of SO_2 formation and energy of activation given.
12	Fe_2O_3	Solid-Gas												CA-44-P-2716a	Fe_2O_3 used as finely divided powder suspended in the gaseous mass. Oxidation carried out under pressure
13	Fe	Solid-Gas							*0.176-2.44 m/sec	*0.43-0.586 sec	*10-14%	*9-18.5%		CA-61-11643e	Preliminary oxidation on fluidized bed of Fe catalyst described. Particle size=0.80 - 1.30 mm. *Dimensional economics given.
14	Fe_2O_3	Solid-Gas												CA-62-8658g	Catalytic activity of Fe_2O_3 in the presence of H_2O discussed.
15	Fe_2O_3	Solid-Gas	250°C											CA-63-P--14405g	Finely divided (<6μ) Fe_2O_3 is sprayed into flue gas stream. Fe_2O_3 and SO_3 recovered at 500°C
16	Fe_2O_3	Solid-Gas	650-720°C		*Water Glass			*720 cm^2/cm^3	*5730-17190 hr^{-1}		*7-12%	*9-14%	*25-30%	CA-66-69286c	Method of preparing catalyst described. Particle diam.-0.75 mm

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CATALYST-IRON

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
17	Fe_2O_3	Solid-Gas	350-450°C								3-4%		95%	CA-66-P-87178y	Process of SO_2 recovery from flue gas described
18	Fe_2O_3	Solid-Gas	100-600°C		Ag									CA-66--108709e	Influence of Ag carrier and doping with Pd and Hg on energy of activation discussed
19	Fe_2O_3	Solid-Gas		Cr,Mn,V, or Zn oxides										CA-24-2556b	Method of preparing catalyst given in supplementary reference
20	Fe_2O_3	Solid-Gas									7%			CA-31-4882f	Mechanism of reaction via $Fe_3(SO_4)_4$ given
21	Fe Pyrite cinders	Solid-Gas									*12%			CA-61-2522d	Stationary and fluidized Fe catalyst layers rate constants determined. *Equations given for making various calculations
22	Fe_2O_3	Solid-Gas												CA-65-9786d	Degradation of catalyst during operation discussed
23	Fe_2O_3	Solid-Gas												CA-68-53714w	Radical theory of active oxides discussed
24	Fe_2O_3	Solid-Gas												CA-68-80802e	Concentration gradients near catalytic surface discussed
25	Fe_2O_3	Solid-Gas											up to 40%	CA-51-9122h	Oxidation of SO_2 catalyzed by Fe_2O_2, Cr_2O_3 and coal ash, fire clay and glossy slags in combustion space of slagging bailers investigated
26	Fe_2O_3 Pyrite cinders	Solid-Gas	500-650°C										93.44% 90.34%	CA-53-3621a	By products of H_2SO_4 prod. Used as catalyst.

CATALYST-IRON

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
27	Burned Pyrite (H_2O 15.6, Fe 56.15, S 3.68, Cu 0.63%)	Solid-Gas		650°C					300 l/l cat-hr.		6.8%		25atm P=76% 100atm=95%	CA-28-4184[4]	Grain Size = 3.5 mm Data given and apparatus described for oxidation of SO_2 under pressure
28	Fe deriv.	Solid-Gas		Zeolite										CA-23-(P)-1018[5]	Method of preparing contact mass described
29	Fe_2O_3	Solid-Gas												CA-35-3883[4]	Mechanism of oxidation on oxide catalysts discussed
30	Pyrite cinders	Solid-Gas	680°C						lin.vol =0.056 m/sec		7-9.5%	11.5-19.5%	>40%	CA-61-5227h	Mechanically stable catalyst described (consumption 2-3%/month)
31	Fe_2O_3 cinders	Solid-Gas												CA-61-6823a	Apparatus for recovery of H_2SO_4 and fresh Fe_2O_3 from spent Fe_2O_3 is described
*32	Fe_2O_3	Solid-Gas												CA-53-13753f	Thermodynamics of Fe_2O_3, Pt, N_2O_3, and V_2O_5 catalytic oxidation compared.

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CATALYST - CHROMIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1	Cr_2O_3	Solid-gas	450°C	SnO_2		Cr_2O_3-10%							50%	CA-53-21103e	Theory of mixed catalysts was discussed. Maximum activity did not coincide with max. surface area.
2	Cr_2O_3	"	350-600°C	SnO_2 0-100%		0-100%			200-1200		7%		63.5%	CA-53-21104a	The reaction $SO_2+O_2=SO_3$ was studied in the presence of carelysts SnO_2 and Cr_2O_3 contg. 0-100% SnO_2.
3	Cr_2O_3	"	350-550°C	SnO_2							2-14%	2-19%		CA-53-21104c	With increase of the SnO_2 content the activity curves of the catalysts go through 2 max. and a min. The most active catalysts were those contg. 2.41% and 33.13% SnO_2.
4	Cr_2O_3	"	550°C 600°C	Al_2O_3	Al_2O_3-90% Al_2O_3 - 84%	Cr_2O_3-10% Cr_2O_3-12% SnO_2-4%					7%		55% 60%	CA-59-2207g	Cr_2O_3 catalyst with Al_2O_3 support is mixed in different proportions and their effect on oxidn. of SO_2 studied.
5	Cr_2O_3	"												CA-59-8161a	Cr_2O_3 is doped with other metal oxides.
6	Cr_2O_3	"												CA-61-12681b	Catalytic oxidn. of SO_2 to SO_3 and its temp. dependence were measured dynamically on doped and undoped Cr_2O_3 contacts.
7	Cr_2O_3	"		SnO_2, TiO_2, Al_2O_3	SnO_2, TiO_2, Al_2O_3									CA-62-11187c	Effects of additives on Cr_2O_3 catalyst for the oxides of SO_2 described.
8	Cr_2O_3	"	550°C		Al_2O_3	Cr_2O_3-10-14%							80%	CA-66-108674z	Oxidn. of SO_2 on non-modified chromia-alumina catalysts were studied with different comps.

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	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
9.	Cr_2O_3	Solid-gas		Sn comp'd										CA-12-P-83[7]	Catalytic material consists of an active basic compound of Sn and voluminous free Cr oxide.
10	$Cr(OH)_2$	"		Base		Cr hydro-oxide hydro-gel								CA-25-P-2817[7]	Method of H_2SO_4 production described.
11	Cr_2O_3 " "	"	450-460°C 515°C "	SnO_2 " "	SiO_2 " "				vel. vol. =100 vel. vol. =145				96.8-97.0% 95% 93-94.8%	CA-29-2669[1]	Preparation of catalyst described Cr catalyst more resistant to poisoning than the V-catalysts.
12	Cr_2O_3 (I) Cr_2O_3 (II)	"	550°C 450°C	Al_2O_3 SnO_2					vel. vol. =145 vel. vol. =31-84		6.4-8.9%		90% overall 96% 88-99%	CA-29-5999[7]	Two catalytic chambers used. Preparation of catalysts and lab apparatus described.
13	Cr_2O_3	"		SnO_2 +BaO and Be_2O_3										CA-30-3601[1,4]	CaO, MgO, SiO, ZnO, Al_2O_3, Bi_2O_3, MnO_2, NiO, CoO, and CuO were found to have negative catalytic effect when added to Cr_2O_3-SnO_2 BaO and Fe_2O_3 containing catalysts are more active than basic Sn-Cr.
14	Cr_2O_3	"	450-550°C	SnO_2-BaO										CA-30-3601[5]	Poisoning of catalyst by As H_2O, and HCl compared with that of V-Sn catalyst. At 550°C both catalyst are immune to As poisoning.
15	Cr_2O_3	"				Cr_2O_3 gel								CA-31-2363[4]	Preparation of Cr_2O_3 gel described.

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4 OF 4

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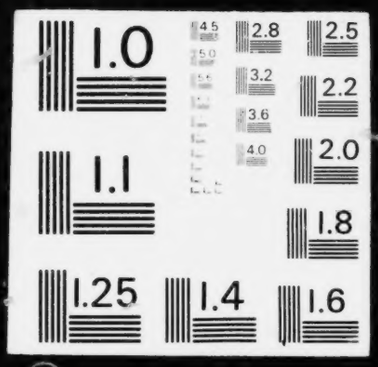

CATALYST - CHROMIUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
16	Cr_2O_3	Solid Gas	320-635°C	SnO_2+ $Ba(NO_3)_2$ or $BaSO_4$	Porcelain									CA-31-4126[3]	Effect of carriers and diluents on energy of activation and the value of the dispersion coefficient discussed.
17	Cr_2O_3 or chrome ore	"											up to 40%	CA-51-9122[2]	Oxidation of SO_2 catalyzed by Fe_2O_3, Cr_2O_3 and coal ash, fire clay and glassy slags in combustion space of slagging boilers investigated.
18	Deriv. of Cr	"		zeolite										CA-22(P)-10185	Method of preparing contact mass described.
19	Zeolite containing Cr			Mr,Be,A,I Me.Cu.Zr. Zn,Pb,Ag, Ce,B and rare earth	Zeolite containing Al. Be. Cd, Zr,Zn or Ti.									CA-23(P)-4865	Details of catalyst preparation
20	Zeolite containing Cr *and V	"		*450-600°C	Zeolite containing K	Zeolite containing SiO_2 and catalytically active metal compounds	*Zeolites containing Cr+V				*7%			CA-23(P)9402	Preparation of catalyst described.
21	Cr_2O_3	"												CA-35-3883[4]	Mechanism of oxidation on oxide catalyst discussed
22	Cr hydrogel	"		slightly soluble base	hydrogel									CA-25-P-5258[5]	Preparation of catalyst described.
23	Cr_2O_3	"												CA-34-3026[7]	Contact properties of Cr_2O_3 discussed. A comment on CA-31-2363[4] is made.

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CATALYST - CHROMIUM

	Catalyst	Type of Catalysis	Temp	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
24.	Cr_2O_3	Solid gas			Ni, Al, or Mg-silicates									CA 65-14481e	Specific surface area, effective pare radius and other adsorption properties were investigated.

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CATALYST - PLATINUM

	Catalyst	Type of Catalysis	Temp	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1	Platinized Pt	Solid-gas	410-50°C										99.6%	CA-51-13541e	On platinized platrone 75.7% SO_2 was oxidized.
2	Platinized Ni	"	150-550°C	Ni	Ni-skeleton platinized asbestos	Pt-1.29% "								CA-55-14973c	Effect of temp. was studied for the oxidn. of SO_2.
3	Pt	"												CA-62-10061	The possibility of electrochemical oxidn. of SO_2 by electrolytic O_2 was studied.
4	Pt	"	500°C											CA-64-4318f	The activity of the Pt catalyst decreased when the catalyst was + ley polarized, and increased when it was -vley polarized.
5	Pt	"	20°C											CA-56-10906c	Data indicate that the actual catalytic act is the interaction of SO_2 with O_2 adsorbed on the active centers of the catalyst.
6	Pt	"	550-674°C								2.7-9%			CA-57-15606a	Kinetics of the process $SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$ was studied in the state of chemical equilibrium on a Pt catalyst by the aid of radioactive S.
7	Pt	"		SiO_2										CA-55-7002f	Sorptive catalytic process of oxidation of SO_2 on Pt catalyst was studied.

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CATALYST - PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
8	Platinum (from $PtCl_4$)	Solid-Gas	438-464°C		Silica Ge									CA-30-P-3182-5	Preparation of catalyst is desired.
9	Platinum	"			Sillimanite, bonded by Et Silicate									CA-43-8074c	Method of preparing catalyst described.
10	Pt black	"	400°C		Asbestos	5g			80cc/min		40%	60%	96-97%	CA-12-1864-1	Efficiency of Pt black compared to that of Rh black.
11	Pt	"			Silica Gel *Asbestos						*8%		*86-96%	CA-23-5278-10	Platinum deposited on silica gel is more efficient than on asbestos. *1 part Pt converts to 450 parts SO_2 to SO_3/24 hrs.
12	Pt	"	360-500°C		Silica Gel		19-118 pore diam. <40Å							CA-29-2830-5	Percentage yields as a function of porosity determined.
13	Pt	"	350-475°C >475°C	Al_2O_3 12-14% SiO_2 88-86%					Vol. Ve = 54 73		6-7.5%		96-97%	CA-28-5998-3	Waste from $AlCl_3$ Industry used as carriers for Pt catalyst.
14	Pt	"			Fe_2O_3	0.024-0.093%			26-105		6.2-8%		92.3-96.5%	CA-31-4063-2	Fe_2O_3 made mechanically stable by adding Sol. glass.

CATALYST - PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
15	Pt	Solid-Gas	*410°C		Silica Gel	1% Pt			*2500 l/l-hr		*6%		Before HNO_3 treatment 76% After 92.8% *Before oxalic acid treatment 86.4% After 97.8%	CA-Y1-P-70664 (Two patents)	Method of activation and regeneration of Pt catalysts described.
16	Pt black	"	150-60°C												Reaction near the critical point of SO_2 investigated.
17	Pt	"			Silica Gel									CA-44-7637e	Grain size:150μ diam. Variation of reaction rate with flow rate through fluidized bed studied.
18	Pt	"	350-480°C		Cylindrical Pellets (1/2") Al_2O_3				Mass vel.= 147-514 lb/hr. sq. ft.					CA-45-937h	Internal diam. of reactors 1.5 in. The importance of diffusion was determined by measuring the rate of oxidation in a flow reactor operated at various mass velocities.
19	Pt	"			1/8" Al_2O_3 pellets	0.2% Pt			Mass Vel.= 147-512 lb/hr. (sq. ft. of empty reactor area)					CA-45-6437c	Design of fired-bed catalytic reactor with regards to temp. gradients and mass velocity was described.

CATALYST - PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
20	Pt	Solid-Gas	360-430°C		Silica ge	0.2% Pt	100Å	30 sq. m/g.			3%	(97% air)		CA-46-9961c	10^2K/per unit surface area=0.35
	"		360-440°C		" "	0.5% Pt	40Å	73 sq. m/g.			"			"	" " " " " =0.21
	"	"	427-500°C			Spongy Pt	16500Å	0.17 sq. m/g.			"	"		"	" " " " " =0.21
	"	"	427-530°C			0.2 mm dia Pt wire		(0.5-2) x 10 sq. m/g.			"			"	" " " " " =0.32
	"	"	427-490°C			Pt net from 0.09 mm wire		"			"	"		"	" " " " " =0.48
	"	"	400-515°C			Pt foil 0.2 mm thick		"			"	"		"	" " " " " =1.80
															Specific catalytic activity of metallic platinum measured.
21	"	"	350-450°C		Silica ge	0.05-4.0%			15-180	lb/hr	"	"	(?)10-40%	CA-47-6234i	K values calculated for various gas flow rates and degree of conversion. Compared with Pd.
	"	"	300-400°C		" "	8% (Crystaline Pt)			"		"	"			
22	"	"	450°C		Nichrome wire (spiral)	0.1% Pt			Low not shown				Near 100%	CA-66-9826lu	Use of Pt-plated Nichrome wire catalyst described
23	"	"	460°C											CA-21-3106[2]	Deleterious effect of Os, Rh and Ir on Pt catalyst investigated
24	"	"	*300°C										*15%	CA-22-4332[9]	Poisoning of Pt catalyst by As.
25	"	"												CA-33-8934[2]	Effect of CO on catalytic activity investigated. No effects observed.

CATALYST-PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
26	Pt	Solid-gas	300-600°C			Pt Sponge								CA-34-7169[1] CA-35-7811[4] CA-41-4366[5]	Mechanism of SO_2 oxidation investigated with heavy O.
27	"													CA-39-3719[2]	Relation between reaction order and energy of activation discussed for direct and inverse reactions.
28	Pt black	"												CA-39-5160[6]	Design of reactor given.
29	Pt	"	*380°C	*Fe	*Silica gel	*0.3-0.8%			*100 lb/hr		*6%	*21%	*85-92%	CA-41-P-577a	Method of activating catalyst described-*using Fe.
30	"	"												CA-41-29721	Mechanics of SO_2 oxidation reaction discussed.
31	"	"												CA-47-4180e	Rate data given for two Pt catalysts, different sizes.
32	"	"				Pt wire 0.04-0.06 mm thick *Woven into net								CA-49-P-7155e	Method of preparing macro-crystaline catalytic structure described.

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CATALYST-PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
33	Pt	Solid-Gas			Al_2O_3 gel									CA-51-5522i	Effect of variation of type of Al_2O_3 gel support discussed
34	"	"	360-530°C		or SiO_2	Pt wire foil and screen Pt (*0.001-0.5%) *Spongy Pt		*Silicagel (3-7)x10^5 cm^2/g Spongy Pt 1.7x10^7 Wire 10.2-20.6 Screen 22.6 Foil 6.9			*1-6.5%			CA-51-9276c	Specific catalytic activity and activation energy determined. *Activation energy=23 KCal/mole.
35	"	"												CA-52-17922i	Specific catalytic activity discussed
36	"	"				Pt gauze								CA-55-25433e	Reaction rates for forward and reverse reaction and energy of activation calculated.
37	"	"	424-440°C											CA-64-5801g CA-65-11396f	Mechanism of oxidation of SO_2 followed by means of labelled S.
38	"	"												CA-65-4707d	Pt-catalyzed SO_2 oxidation used to demonstrate dynamics of a surface catalyzed system

CATALYST - PLATINUM

	Catalyst	Type of Catalysis	Temp	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc	O_2 Conc	Conversion Efficiency	Reference	Remarks
39	Pt	Solid-Gas												CA-37-6416[7]	Catalyst consisting of Pt on the surface of the carrier grains were studied, along with Cs-V and Fe-Cu-V catalysts
40	"	"	450-800°C						$15 m^3/hr$		66%	34%	60%	CA-41-P-8410	Method of preparing SO_3 described
41	"	"			Asbestos Silica Gel									CA-42-3918d	Data summarized on particle size and porosity and the calculation of overheating coefficients for several catalysts used for the oxidation of SO_2
42	"	"	~520°C		Glass								50%	CA-60-4851a	The effect of pressure (4 atm) on the catalytic oxidation of SO_2 was investigated. Pressure has a small influence on porous carrier catalysts.
43	"	"	*400-450°C			Platinized nichrome wire spirals. *Platinized platinum			*68-458		*7%		*69.4-76.7 %	CA-52-16851a	*Effects of heat-treatment and space velocity on activity of Platinized Nichrome and platinum investigated.
44	"	"		Mn 5% (or Fe, Ni, Al, Cu, Bi, Ma, Be, W Sn, Cr)	Clay containing Al_2O_3-SiO_2 Silica gel									CA-28-P590[4]	Methods of preparing catalysts are given.

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CATALYST-PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
45	Pt	Solid-Gas		Mn, Be, Al, Ti, Fe, Cu, Zr, Zn, Pb, Ag, Ce, Ni, Co, B and rare earths	Zeolite containing Al, Be, Cd, Zr, Zn or Ti									CA-23(P)-4867	Details of catalyst preparation given.
46	"	"			Kieselguhr and SiO_2									CA-25(P)-1047	Support material described.
47	Silicates of Pt or Pb group metals	"			Kieselguhr pumice or gaucosil									CA-26(P)-2022[6]	Methods of catalyst preparation described
48	Pt	"												CA-31-3217[9]	Kinetics of catalysis compared with that of V-catalyst
49	"	"												CA-35-3883[4]	Mechanism of catalytic oxidation discussed.
50	"	"												CA-40-2943[8]	Kinetics discussed

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CATALYST - PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
51	Pt	Solid-Gas	~520°C		Glass									CA-60-4851a	Effect of pressure on catalytic activity discussed.
52	"	"	Max. 525°C								*8%	*12%	*50-98%	CA-19-2111	Two types of converters providing for gas cooling to achieve max activity described
53	"	"	*416-460°C		Asbestos						*9%		*93-97%	CA-21-2962[9]	Influence of reaction rate on operating conditions in contact process discussed.
54	"	"												CA-29-P-565[3]	Regeneration of catalyst described
55	"	"												CA-29-P-5610	Regeneration of catalyst described
56	Pt compounds	"		Fe compounds	Silica gel									CA-34-P-6028[8]	Method of preparing catalyst is described.
57	Pt	"	425°C		Asbestos						*0.3-0.7%	*1-21%		CA-37-4294[7]	Rate equations investigated *(Data obtained from #53 above)
58	"	"			$BaSO_4$	5-8%								CA-47-5233e	Adsorption isotherms obtained for various $BaSO_4$ + Pt mixtures

CATALYST- PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
59	Pt	Solid-gas												CA-56-5438h	Relation between catalytic activity of C and P investigated electrochemically.
60	"	"												CA-60-2367d	Entropy calculations made on oxidation of SO_2 on Pt catalyst
61	"	"			Al_2O_3									CA-61-P-75c	Preparation of catalyst for oxidation of exhaust gas with high stability.
62	"	"			Ceramic balls 90% Al_2O_3 10% Clay									CA-61-P-75d	Preparation of Pt catalyst on ceramic balls by flame-spraying.
63	Pt net (Electrically charged)	"	500°C											CA-63-7682f	Effect of application of electric field to heated cylindrical Pt net and effect of annealing on catalytic activity investigated. (Neg. charge increases, pos. charge decreases activity.
64	Pt	"			Al_2O_3									CA-65-P-6360d	Method of catalyst preparation described.

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CATALYST - PLATINUM

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
65	Pt	Solid-gas			SiO_2 Charcoal	3% 5%	<50° A							CA-68-72717r	Examination of structure of supported platinum catalysts by electron miscroscopy described.
66	"	"	395-405°C											CA-67-47604y	Mechanism investigated.
*67	"	"	450-650°C		Silica gel Asbestos or calcined $MgSO_4$	1.5%					33%	17%	47.9-96.2 %	EI-58-1228	Kinetics and mechanism reviewed. Preparation of catalyst, poisoning, and regeneration discussed. Pt compared with IR and Pd.
*68	"	"		P_2O_5 or MoO 0.5-3.0%	Asbestos, silica, silica & al or $MoSO_4$								98%	CA-66-P-4550	Two-stage converter described.
*69	Pt-Pd (75%-25%)	"	489°C		Al_2O_3 or $MgSO_4$	0.6%			6000 vol.		8%		97.2%	CA-42-P-2410	Catalyst preparation described.
*70	Pt-black Rh-black	"	260-603°C 230-662°C		Asbestos fibers	7.5%					4%	60%	50.1-96.8 % 46.2-91.1 %	CA-20-5[9]	Platinum black compared with rhodium black.
*71	Pt	"												CA-53-13753f	Thermodynamics of Pt, N_2O_3, Fe_2O_3 and V_2O_5 catalytic oxidation compared.

CATALYST - CARBON

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1	Carbon semi-coke	Solid-gas									2-3%			CA-62-P-1357f	Poor conversion of SO_2 was mitigated by having the catalyst retain H_2SO_4.
2	Carbon	"												CA-62-8425c	The mechanism of catalytic oxidn. on activated carbon.
3	Carbon	"	20°C					974-1289 m^2/g						CA-63-3662h	The contribution of carbon free radicals in the SO_2 oxidn. at 20°C was examined.
4	Active char.	"	65-80°C							10-20sec			30%	CA-63-8071e (see EI-66-3001 card)	With continuous or intermittent downwashing. Dil H_2SO_4 could be recovered.
5	Coal	"												CA-65-P-18202e	Modifications of multistage scrubbing tower for removing SO_2 from the flue gases by wet catalytic oxidn. to H_2SO_4 over coal are described.
6	Carbon	"	20°C					265-342 m^2/g						CA-65-19351d	Correlation between the concen. of free radicals of carbon and its catalytic activity in H_2S and SO_2 oxidn. processes was studied.
7	Activated Charcoal	"		Na_2CO_3										CA-17-3271[8]	Difference in source of charcoal as to activity noted. Quantitative measurements given.

CATALYST-CARBON

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
8	Carbon	Solid-Gas	20°C											CA-55-17163d	Catalytic oxidation of SO_2 in presence of H_2O on activated C surface discussed. Good catalyst only in liq. cont. method.
9	Carbon	Solid-Gas	20-150°C											CA-56-48f	Mechanism of oxidation at carbon surface discussed.
10	Carbon	Solid-Gas	20°C											CA-59-67c	Relation between oxidation and the adsorption and desorption isotherms on activated carbon studied.
11	Carbon	Solid-Gas	<220°C											CA-51-8391h	Liquid-contact method employed. Rate of oxidation depends on pressure.
12	Carbon	Solid-Gas	0-60°C											CA-56-10963e	Effect of temperature on conversion in liquid-contact method.
13	Carbon	Solid-Gas		Sulfur							1-5%			CA-61-2758c	Various grades of carbon and methods of activation for adsorption and oxidation of SO_2 compared. Influence of conc., particle size and surface area investigated.
14	Activated coal or charcoal	Solid-Gas					Pore radius <20A	552-892 m^2/g	Linear rate = 15-20 cm/sec		0.25%	8%	75-92%	CA-61-P-3961c	Anthracite coal gives better conversion than charcoal or peat coal.

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CATALYST-CARBON

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
15	Carbon	Solid-Gas												CA-56-5438h	Relation between catalytic activity of C and P investigated electrochemically.
16	Carbon	Solid-Gas	40-70°C				11.52Å= rad 0.318 cc/g = vol.	552 m^2/g	1200 1/hr		0.25%	10%	90%	CA-63-P-3925e	Production of H_2SO_4 from gases with low SO_2 concentration described.

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CATALYST-MANGANESE

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1.	Mn-compound	Solid Gas												CA-65-406a	Use of Mn catalysts in removing S compounds from gases reviewed.
2.	MnO_2 from $KMnO_4$ and $MnSO_4$	Solid-Gas												CA-20-P-37862	Method of catalyst preparation described
3.	MnO_2	Solid-Gas											90%	CA-67-P-57063k	100 μ particle size MnO_2 used.

MISCELLANEOUS SOLID CATALYSTS

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1	Metals & Pt-Au alloys	Solid-gas	428-580°C			wires or shavings (0.1mm dia) or plates					1-1.5%	20.8%	50%	CA-50-3863a	Catalytic activity of Pd, W, Pt, Au_2, Pt-Au alloys, Cr, Rh, Ag was evaluated.
2	Pt, V_2O_5, Fe_2O_3	"												CA-55-21499h	Isotherms for the catalytic oxidn. SO_2 + SO_3 are given and the abs. speed of reaction as a function of equil. state is examd. for 3 different catalysts, Pt, V_2O_5 and Fe_2O_3.
3	Com. Na-vanadate	"												CA-56-15395g	Pore structure and D_{eff} of different catalyst specimens were detd. under different temp. conditions, and effects on reaction kinetics calcid.
4	Pt sponge, V_2O_5 & Fe_2O_3	"												CA-56-12355a	Catalytic oxidn. of SO_2 as a function of the residence time of the gases in the reaction chamber was studied.
5	Ion-exchange	"	50-65°C		Vinyl-pyridine				$1m^3$/min	3hrs 10 min	0.15-2.3%	0-6.02%	70%	CA-63-P-2635a	Ion exchange resins were used to oxidize SO_2 in industrial gases to SO_3.
6	Pt or V_2O_5	"	450°C							1.4 sec	0.13%		95%	CA-63-P-1031a	Absorption capacity of C-contg. absorbants for S-contg gases can be greatly increased by the oxidn. of SO_2 to SO_3.

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MISCELLANEOUS SOLID CATALYSTS

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
7	Chromium-Vanadium	Solid-Gas	450°C						Vol.Vel. = 300 Contact vel.= 78.3				95.3%	CA-32-7280f	Method of preparing catalyst described. Energy of activation given.
8	Rh-black	Solid-Gas	610°C		Asbestos	5 g			80 cc/min				91.1%	CA-12-1864-i	Activity compared with that of Pt-black.
9	Pd	Solid-Gas	450-500°C		Silica Gel	0.05-2.1%			8-50 l/hr					CA-47-6234 i	K values calculated for various gas flow rates and degree of conversion. Compared with Pt.
10	Pt-Pd	Solid-Gas	470-500°C		Al_2O_3, $MgSO_4$ Silica Gel or asbestos	0.3-0.6% 10-100% Pt			5000 vol/vol cat/hr		8%		78.8-97.2%	CA-41-P-4625e	Advantage of Pt catalyst containing 20-40% Pd discussed.
11	Pt-Rh	Solid-Gas				Wires 0.04-0.06mm thick								CA-49-P-7155e	Method of preparing macro-crystalline catalytic structures described.
12	Zno SnO_2	Solid-Gas			Clay									CA-17-P-3575g	
13	Rh-black	Solid-Gas			Asbestos Fibers									CA-20-5g	Rh-black compared with Pt-black as catalyst for gaseous oxidation and reduction reactions.
14	$MgSO_4$	Solid-Gas												CA-42-3918d	Data summarized on particle size & porosity & the calc. of overheating coefficients for several catalysts used for the oxidation of SO_2.

MISCELLANEOUS SOLID CATALYSTS

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
15	Cb, Ti, and Ta oxides from Loparite	Solid-Gas		—										CA-34-P-1588-6	Preparation of Catalyst described.
16	Re	Solid-Gas												CA-45-6143a	As a catalyst, colloidal Re is more effective than powdered Re.
17	n-type semiconductors (WO_3, Fe_2O_3, SiO_2, As_2O_3, V_2O_5)													CA-50-8302b	Reaction mechanism discussed.
18	Deriv. of Fe, Cr, Ni, Co, Cu, W, V, U, or Mo	Solid-Gas		Zeolite	Zeolite									CA-22-(P)-1015[5]	Gas containing SO_2 and O_2 passed over catalyst at elevated temperature. Method of preparing contact mass described.
19	V, Mo, W, U, Cr, Mn, As, Sb, Ta, Nb, or Bi	Solid-Gas	*430-550°C	Alkali Metals	Zeolite containing Al, Be, Cd, Zr, Zn, Ti (Be water-glass, zeolite, Kieselguhr, etc.)	Primarily V_2O_5, in various mixtures, was used 5-10%					*4-6%		*96-98.5%	CA-23-(P)-486[7]	Details at catalyst preparation given. *Particle size <60μ.
20	V, Mo, W, U, Cr, Mn, Ti	Solid-Gas	*450-600°C	Zeolite containing K	Zeolite containing SiO_2 & catalytically active metals	*Zeolite containing V and Cr or V and Ag					*7%			CA-23-(P)-940[2]	Preparation of catalyst described.
21	Silicates of Pt, V, Fe or Mn	Solid-Gas			Kieselguhr, pumice or glaucosil									CA-26-(P)-2022[6]	Method of catalyst preparation given.

MISCELLANEOUS SOLID CATALYSTS

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
22	Mixture of CbO_5, Ta_2O_5 and TiO_2 from Loparite	Solid-Gas												CA-32-2295[5]	Use of this catalyst in contact process described.
23	Pt, V_2O_5+ K_2SO_4, Na_2SO_4, SiO_2, CrO_3, Fe_2O_3, CuO	Solid-Gas												CA-35-3883[4]	Mechanism of oxidation on oxide catalysts discussed.
24	ZnO, NiO and V_2O_5	Solid-Gas												CA-57-1101	Mechanism discussed.
25	CaO, $Ca(OH)_2$, $CaCO_3$, $CaHCO_3$, or similar Mg, Sr, Ba compounds	Solid-Gas	350-550 °C	0-25% NaOH, Na_2O, Na_2CO_3, KOH, K_2O, K_2CO_3, or $KHCO_3$	Al_2O_3, SiO_2-Al_2O_3 or diatomaceous earth				250-2500 m^3/m^3 catalyst/hr		<0.1%	<0.5%	<80%	CA-64-(P)-6370d	Removal of sulfur compounds from coke oven gases and method of catalyst preparation described.
26	Al_2O_3	Solid-Gas				97%								CA-66-P-59305u	Regeneration of activity discussed.
27	Cr oxide, Cu oxide, and/or Mn oxide	Solid-Gas	1st - 400-500°C 2nd - 500-800°C		Silicates									CA-68-P-93771y	Two-step process for purification of exhaust gases containing S-compounds described.

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CATALYST-IRON (Liquid-Phase)

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1.	$FeSO_4$	Liquid-Gas	*20-90°C		Water	*3-20% $FeSO_4$			10-1./hr		*3%	*3-15%		CA-50-1509h -6992h	Oxidation of SO_2 in solution of iron sulfate described. Mechanism discussed
2.	Fe	"												CA-50-1444c	Mechanism of oxidation of SO_2 by dissolved O in concentrated solutions of basic $Al_2(SO_4)$ and catalyzed by small concentrations of iron compounds discussed.
3.	Fe salts	"												CA-27-5899[4]	Catalytic oxidation by ionized solutions of heavy metals described.

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CATALYST-MANGANESE (Liquid-Phase)

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc	Conversion Efficiency	Reference	Remarks
1	$MnSO_4$ Solutions	Liquid-Gas												E_I(1965)2465	Rate of reaction of SO_2 and O_2 in aqueous $MnSO_4$ solution investigated.
2	$MnO.Mn(OH)_3$ $KMnO_4$ solutions	Liquid-Gas												CA-30-2090[5]	Mechanism of oxidation of SO_2 in solution of Mn salts. Oxidation by ozone in presence of Mn salts also discussed.
3	$MnSO_4$ solutions	Liquid-Gas												CA-30-2474[3]	Kinetics discussed.
4	$Mn_2(SO_4)_3$ solution	Liquid-Gas												CA-30-3596[2]	Effect of gas flow rates and poisoning by phenol discussed.
5	Mn catalyst	Liquid-Gas	0-20°C											CA-30-3596[6]	Effect of temperature on poisoning of Mn by phenol.
6	$MnSO_4$	Liquid-Gas	0-60°C											CA-30-5732[3]	Effect of temperature on reaction rates and poisoning.
7	$MnSO_4$	Liquid-Gas	20-40°C											CA-30-7019[5]	Effect of poisoning in oxidation of SO_2 by ozone.
8	Mn catalysts	Liquid-Gas												CA-31-1963[3]	Poisoning of Mn catalysts by H_2SO_4 discussed.
9	$MnSO_4$	Liquid-Gas												CA-32-5285[9]	Mechanism of oxidation of SO_2 with O_2 in presence of Mn catalyst studied by optical means.
10	$MnSO_4$	Liquid-Gas												CA-46-2267d	Composition of scrubber liquid in NH_3 scrubbing of flue gas controlled by use of $MnSO_4$ catalyst.

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CATALYST-MANGANESE (Liquid-Phase)

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
11	Mn oxides	Liquid-Gas	45-50°C			8%					0.17%	2.8%	65%	CA-61-P-6657e	Method of H_2SO_4 production from flue gases described.
12	$MnSO_4$	Liquid-Gas	25°C												Concentration of $MnSO_4$ and reaction rate discussed.
13	$MnSO_4$	Liquid-Gas				0.05-1.0%								CA-63-17193d	Effect of H_2SO_4 concentration on catalytic activity of $MnSO_4$ in oxidation of SO_2 by O_3.
14	$MnSO_4$ solution containing Al	Liquid-Gas				0.05% Mn 0.05-5% Al					1-20%			CA-34-P-3889	Method of preparing 40% H_2SO_4 described.
15	$MnSO_4$ solution containing $Al_2(SO_4)_3$	Liquid-Gas		0.15% Al		0.05% Mn								CA-47-3116b	Air oxidation during scrubbing with aqueous solution in a column is described.

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MISCELLANEOUS LIQUID PHASE CATALYSTS

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1	Salts of Fe, Cu or Mn	Liq.												CA-27-5899[4]	Catalytic oxidation by ionized solutions of heavy metals described.
2	Aqueous solution of Al and Mn compounds	Liquid			0.05% Mn 0.05-5% Al						1-20%			CA-34-(P)-3889[1]	Method of preparing 40% H_2SO_4 described.
3	Metallic catalysts	Liquid												CA-65-(P)-5210[b]	Gas is scrubbed with water and treated with a metallic catalyst.
4	NH_3	Liquid												CA-66-108894[w]	Kinetics of SO_2-NH_3-liquid H_2O system discussed.
*5	Iodine or metals (Mn, Cu, Au, Pb, Tl, Fe, Zn, Ni, Co, Sn, As, Ch, V, Mo	Liquid	<100°C		Carbonaceous Adsorbents, Meerschaum and Aluminum Silicates				2000m³/hr		4g/m³			CA-62-P-8706[d]	SO_2 was catalytically oxidized to SO_3 which was absorbed by dilute H_2SO_4.

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MISCELLANEOUS GAS PHASE CATALYSTS

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
1	Oxides of N_2	gas-gas liquid-gas	80-130°C			Equivalent to 7% HNO_3			10cm/sec		4-16%	0.2-15.8%	67-92%	CA-49-42481	The effect of temp. and SO_2 concen. on the conversion of SO_2 to SO_3 was studied for max. liquid spray rates.
2	N_2O in the presence of NO	gas-gas												CA-57-10570c	Decomposition of N_2O at 700°C can be used as a source of O atoms for the oxidation of SO_2.
3														CA-60-218c	The effect of concen. of N_2O_3 and H_2SO_4 in nitrous acids on the conversion of SO_2 in the Kachkaroff process is studied.
4														CA-61-327b	Oxidation of SO_2 with nitrose in packed columns and in sieve plate columns was studied.
5											0.3%			CA-64-17305g	Air concentration 0.3% SO_2 is converted to $(NH_4)_2SO_4$ by NH_3 and O_3.
6	Oxides of N_2	gas-gas	400°C											CA-65-17756f	Reactions $NO_2+SO_2 \rightleftharpoons NO+SO_3$ and $NO_3+SO_2 \rightleftharpoons NO_2+SO_3$ vary with the concentrations of the reactants and with temperature.
7		gas-gas												CA-65-5061f	Absorption rate of SO_2 is the presence of the N oxides was increased by approximately 20-5% in comparison with the absorption rate in the absence of N oxides.

MISCELLANEOUS GAS PHASE CATALYSTS

	Catalyst	Type of Catalysis	Temp.	Weight % Promoter	Weight % Support Material	Weight % Catalyst	Porosity	Surface Area	Gas Flow Rate	Contact Time	SO_2 Conc.	O_2 Conc.	Conversion Efficiency	Reference	Remarks
8	N_2O_3	gas-gas												CA-53-13753i	Thermodynamics of N_2O_3, Pt, V_2O_5 and Fe_2O_3 catalytic oxidation compared.
9	N oxides	gas-gas	700°C											CA-67-23705i	Factors affecting the formation of SO_3 in flame gases discussed.

APPENDIX IV

CAPITAL COST SUMMARY SHEETS

APPENDIX IV

INDEX

PROCESS NAME	Page
Monsanto-Penelec (low temperature effluent)	221
Monsanto-Penelec (high-temperature effluent)	222
Kiyoura-T.I.T. (low temperature effluent)	223
Kiyoura-T.I.T. (high temperature effluent)	224
Rein-luft Process (low temperature effluent)	225
Sulfacid Process (low temperature effluent)	226
Mitsubishi Process (low temperature effluent)	227
T.V.A. Process (low temperature effluent)	228
Callery Process (low temperature effluent)	229

SO_2 REMOVAL FROM FLUE GAS

Category: Existing Power Plant (Low Temperature Effluent)

Capital Cost Estimate Summary

Name of Process: Monsanto-Penelec Flue Gas Rate: 2.5 MMSCFM

MW 1400

		Cost $
1) Purchased Equipment		
	Flue Gas Heater	655,000
	Catalytic Converter	540,000
	Primary Heat Exchanger	1,530,000
	Second Heat Exchanger	2,600,000
	Mist Eliminator	1,850,000
	TOTAL	7,175,000
2) Fixed Capital Cost*		34,081,000
3) Working Capital**		3,408,000
	TOTAL INVESTMENT	37,489,000
4) Capital Requirements $/kW Capacity		26.77

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost

SO_2 REMOVAL FROM FLUE GAS

Category: New Power Plant (High Temperature Effluent)

Capital Cost Estimate Summary

Name of Process: Monsanto-Penelec Flue Gas Rate: 2.5 MMSCFM

MW 1400

	Cost $
1) Purchased Equipment	
Catalytic Converter	540,000
Economizer	1,530,000
Air Preheater	2,600,000
Mist Eliminator	1,850,000
TOTAL	6,520,000
2) Fixed Capital Cost*	30,970,000
3) Working Capital**	3,097,000
TOTAL INVESTMENT	34,067,000
4) Capital Requirements $/kW Capacity	24.33

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost

SO_2 REMOVAL FROM FLUE GAS

Category: Existing Power Plant (Low Temperature Effluent)

Capital Cost Estimate Summary

Name of Process: Kiyoura-T.I.T. Flue Gas Rate: 2.5 MMSCFM

MW 1400

		Cost $
1) Purchased Equipment		
	Flue Gas Heater	655,000
	Converters, Blowers, and Motors	540,000
	Primary Heat Exchanger	1,530,000
	Secondary Heat Exchanger	1,040,000
	Electrostatic Precipitator	1,200,000
	TOTAL	4,965,000
2) Fixed Capital Cost*		23,535,000
3) Working Capital**		2,354,000
	TOTAL INVESTMENT	25,889,000
4) Capital Requirements $/kW Capacity		18.49

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost

SO_2 REMOVAL FROM FLUE GAS

Category: New Power Plant (High Temperature Effluent)

Capital Cost Estimate Summary

Name of Process: Kiyoura-T.I.T. Flue Gas Rate: 2.5 MMSCFM

MW 1400

	Cost $
1) Purchased Equipment	
Converters, Blowers, and Motors	540,000
Economizer	1,530,000
Air Preheater	1,040,000
Electrostatic Precipitator	1,200,000
TOTAL	4,310,000
2) Fixed Capital Cost*	20,430,000
3) Working Capital**	2,043,000
TOTAL INVESTMENT	22,473,000
4) Capital Requirements $/kW Capacity	16.05

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost

SO_2 REMOVAL FROM FLUE GAS

Category: Low Temperature Effluent

Capital Cost Estimate Summary

Name of Process: Reinluft Process Flue Gas Rate: 2.5 MMSCFM

MW 1400

	Cost $
1) Purchased Equipment	
Adsorber	1,100,000
Regenerator	100,000
Heater	195,000
Cooler	110,000
Blowers and Motors	3,936,000
TOTAL	5,441,000
2) Fixed Capital Cost*	25,800,000
Sulfuric Acid Plant	2,800,000
TOTAL	28,600,000
3) Working Capital**	2,860,000
TOTAL INVESTMENT	31,460,000
4) Capital Requirements $/kW Capacity	22.47

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost

SO_2 REMOVAL FROM FLUE GAS

Category: Low Temperature Effluent

Capital Cost Estimate Summary

Name of Process: Sulfacid Process Flue Gas Rate: 2.5 MMSCFM

MW 1400

	Cost $
1) Purchased Equipment	
Venturi Scrubber	3,340,000
Reactors	7,700,000
Blowers and Motors	810,000
Acid Purification and Concentration	1,175,000
TOTAL	13,025,000
2) Fixed Capital Cost*	61,750,000
3) Working Capital**	6,175,000
TOTAL INVESTMENT	67,925,000
4) Capital Requirements $/kW Capacity	48.51

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost

SO_2 REMOVAL FROM FLUE GAS

Category: Low Temperature Effluent

Capital Cost Estimate Summary

Name of Process: Mitsubishi Process Flue Gas Rate: 2.5 MMSCFM

MW 1400

		Cost $
1) Purchased Equipment		
	Absorber	525,000
	Cyclone Separator	791,000
	Electrostatic Precipitator	1,200,000
	Ammonia Scrubber	30,000
	Oxidizing Tower	30,000
	Air Compressor	170,000
	Crystallizing Equipments	1,440,000
	Miscellaneous	200,00
	TOTAL	4,386,000
2) Fixed Capital Cost*		20,790,000
3) Working Capital**		2,079,000
	TOTAL INVESTMENT	22,869,000
4) Capital Requirements $/kW Capacity		16.33

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost

SO_2 REMOVAL FROM FLUE GAS

Category: Low Temperature Effluent

Capital Cost Estimate Summary

Name of Process: T.V.A.-Sulfuric Acid Process Flue Gas Rate: 2.5 MMSCFM

MW 1400

		Cost $
1) Purchased Equipment		
	Evaporator	1,450,000
	Packed Scrubber	7,700,000
	Blowers & Motors	810,000
	Mist Eliminators	1,850,000
	TOTAL	11,810,000
2) Fixed Capital Cost*		56,000,000
3) Working Capital**		5,600,000
	TOTAL INVESTMENT	61,600,000
4) Capital Requirements $/kW Capacity		44.00

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost

SO_2 REMOVAL FROM FLUE GAS

Category: Existing Power Plant (Low Temperature Effluent)

Capital Cost Estimate Summary

Name of Process: Callery Chemical ~~Company's Process~~ Flue Gas Rate: 2.5 MMSCFM

MW 1400

		Cost $
1) Purchased Equipment		
	Flue Gas Heat Exchanger	2,140,000
	Catalytic Reactor	300,000
	Absorber-Stripper	220,000
	Furnace	300,000
	Gas Cooler	65,000
	Sulfuric Acid Absorber & Mist Eliminator	40,000
	Acid Cooler	100,000
	Fan and Blower	63,000
	TOTAL	3,228,000
2) Fixed Capital Cost*		15,300,000
3) Working Capital**		1,530,000
	TOTAL INVESTMENT	16,830,000
4) Capital Requirements $/kW Capacity		12.02

* Langs factor applied; 4.74 for fluid process plants
**10% of the fixed capital cost